ELECTROCHEMISTRY AT THREE-PHASE ELECTRODES

Rubin Gulaboski
FACULDADE DE CIENCIAS,
DEPARTAMENTO DE QUIMICA, PORTO

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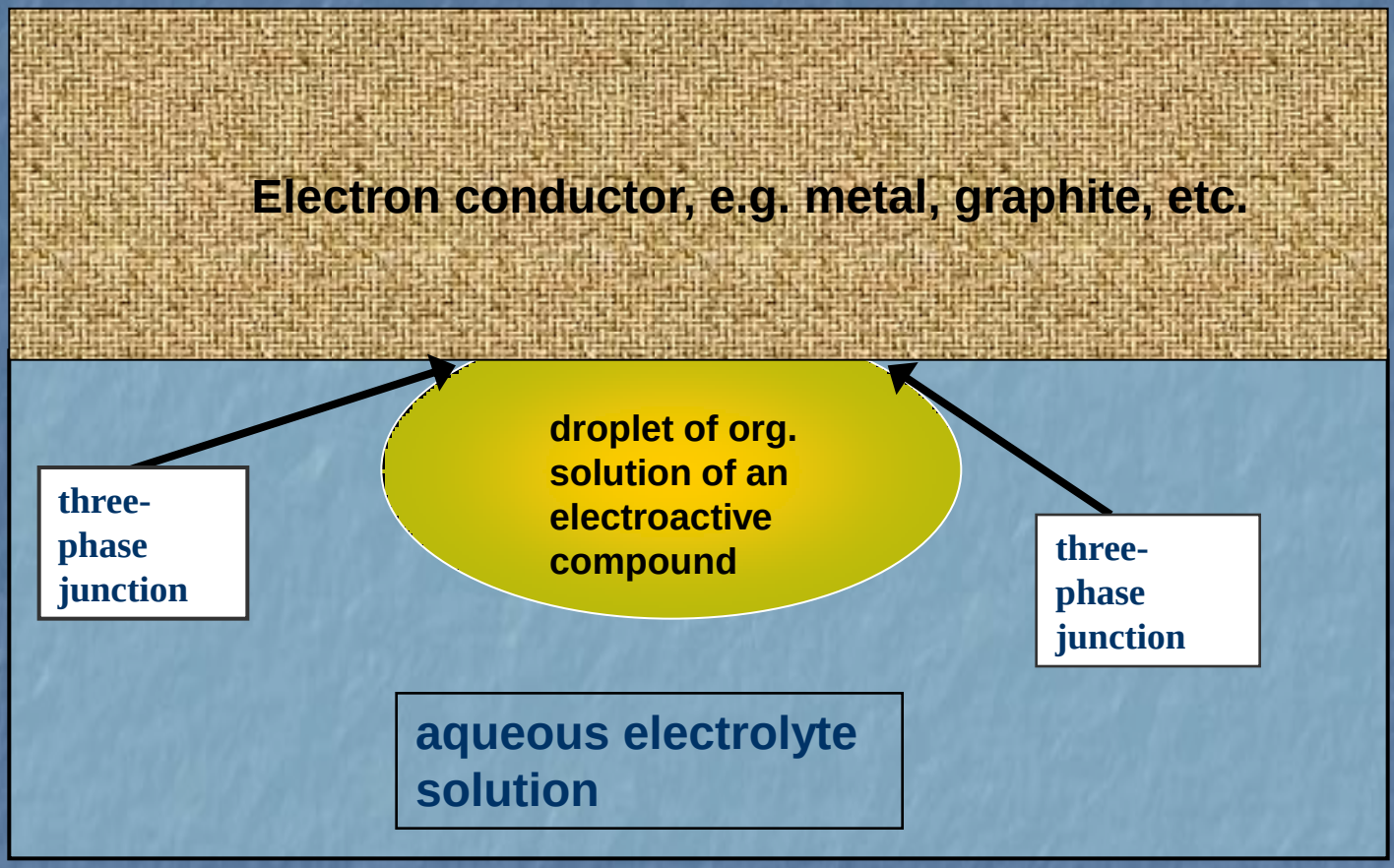
GREIFSWALD-ONE CITY AT THE EDGE OF NOWHERE
(NORTH-EAST GERMANY)

THREE-PHASE ELECTRODE



APPLICATION of the **THREE-PHASE ELECTRODE** for

-STUDYING THE ***ION TRANSFER*** PROCESSES ACROSS THE LIQUID|LIQUID INTERFACES

-Measuring the ***THERMODYNAMICS*** OF ION TRANSFER

-MEASURING the ***KINETICS*** of ION TRANSFER

-MAKING ***ELECTROCHEMICAL SENSORS*** for BIOLOGICAL COMPOUNDS

-***Synthesis of Ag-Nanoparticles*** at L|L interface (cathalysis)

APPLICATIONS of Ion Transfer Processes

Phase-Transfer Catalysis

Kinetics of Ion Extraction

Electrochemical Sensors

Drug Delivery in Pharmacology

Standard Gibbs energy of transfer **ΔG^{o}-the main physical parameter deduced from the studies of the ion transfer across two immiscible solvents**

- **measure of the strenght of solvation interactions**

$$\Delta G_i^{\theta(A\rightarrow B)} = E_i\,\mathrm{solv(B)} - E_i\,\mathrm{solv(A)}$$

$$\Delta G_i^{\theta(w\rightarrow o)} = -\Delta_w^o \varphi_i^\theta zF$$

Link between **partition coefficient *P***

and **standard Gibbs energy of transfer**

$$P_i = \exp\left(-\frac{\Delta G_i^{\theta(w\rightarrow o)}}{RT}\right) \qquad P_i = \frac{a_{i(o)}}{a_{i(w)}}$$

Importance of the partition coefficient

Measure of the **lipophilicity** of the compounds

Prediction of the transport through membranes

Toxicity

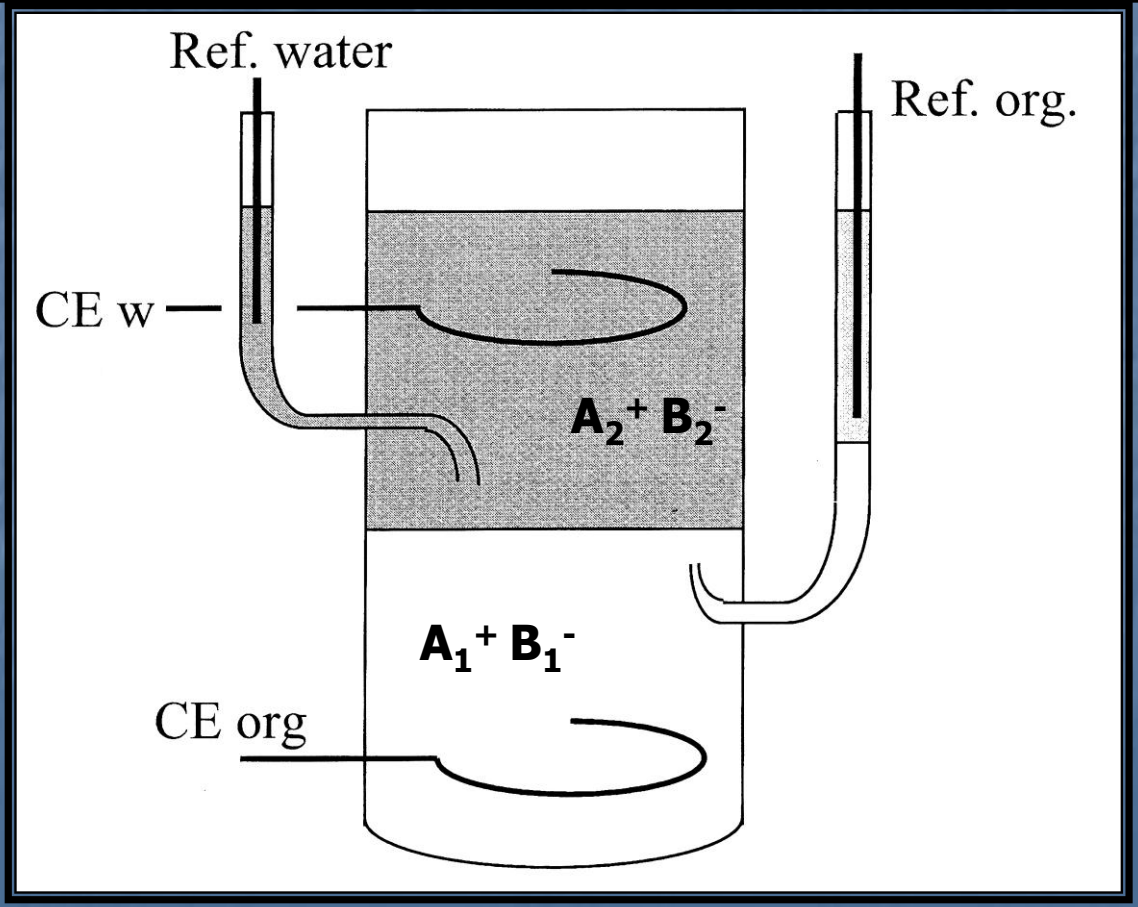
QSA-Relationships and QSP-Relationships

Drug design

The determination of log*P* of neutral solutes almost a routine work -with the help of various partition techniques

The determination of log*P* of single ions requires potentiostatic controlling of the interfacial potential established at the liquid|liquid interface due to the ionic partitioning

Until recently: **Four electrode measurements** (cyclic volatmmetry) at the ***Interface between two immiscible electrolyte solutions (ITIES)*** *was the only technique for measuring the* ***lipophilicities of ions***

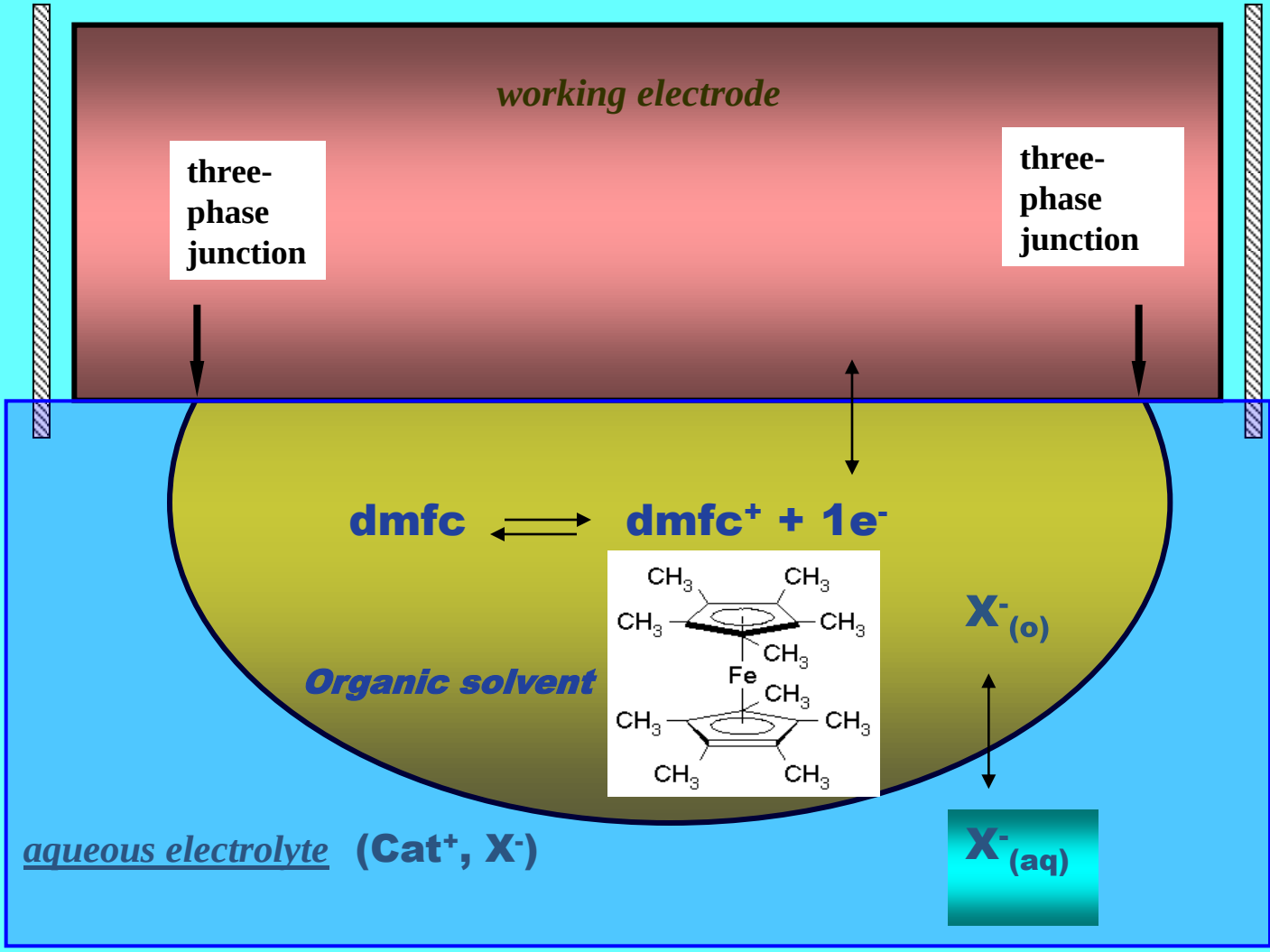


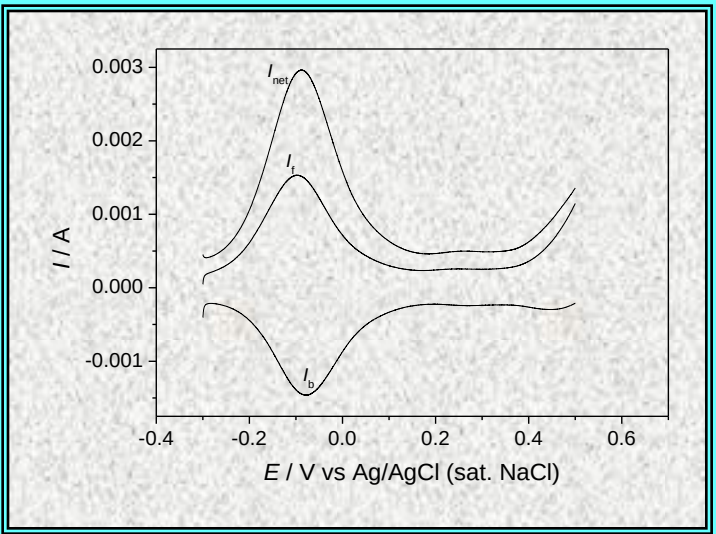
Three-phase electrode approach

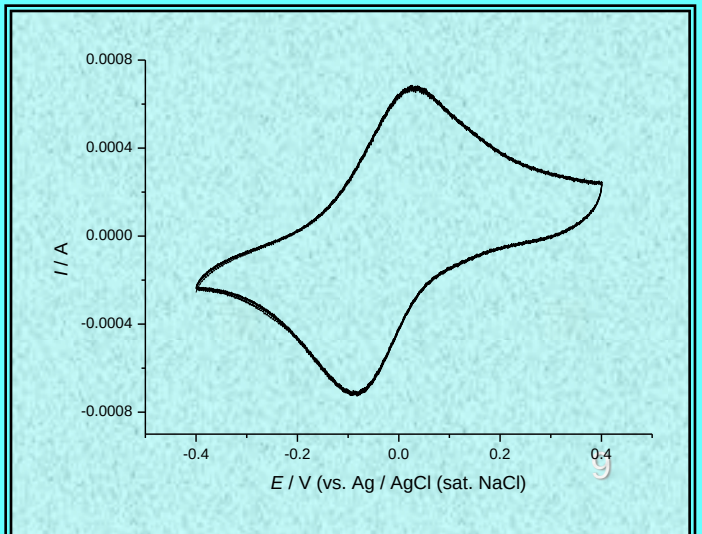
Scholz et all, *Electrochem. Commun.* *2*, **2000**, 112.
(**Awarded for „The Best Cited Paper" in 2003**)

reference electrode

counter electrode

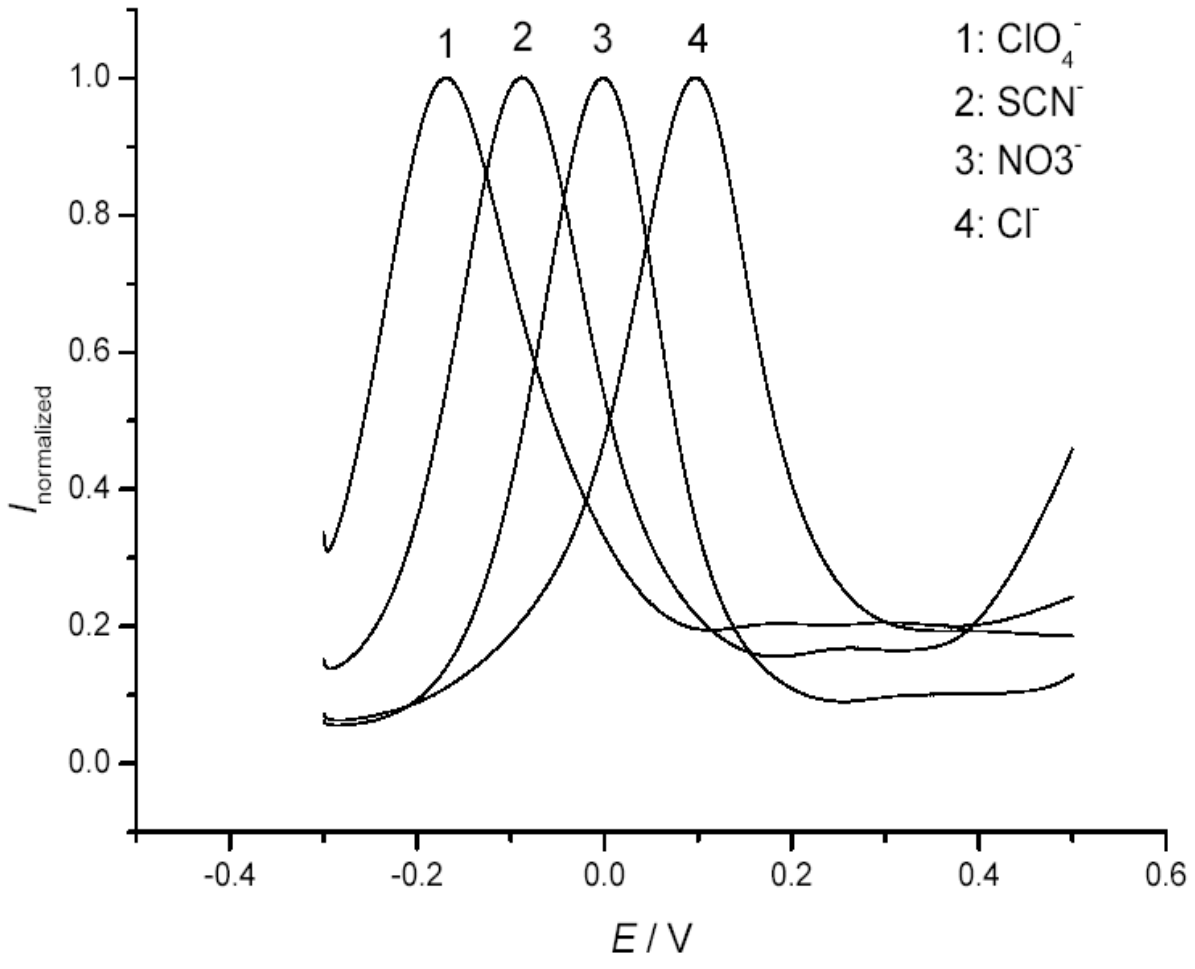




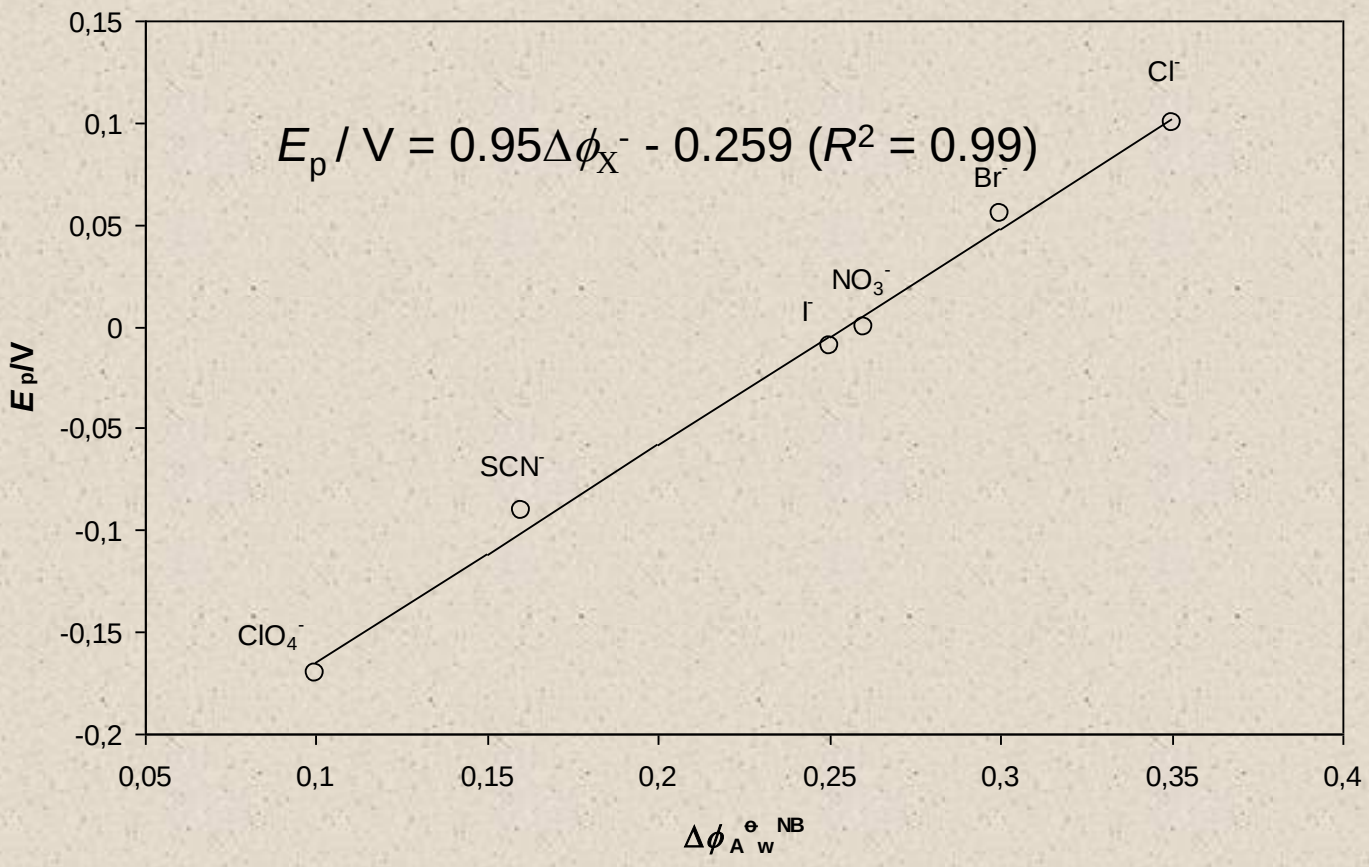


$$dmfc(o) + A^-(w) \Leftrightarrow dmfc^+(o) + A^-(o) + 1e^-$$

$$E_f = E^{\theta}_{dmfc^+/dmfc(o)} - \frac{RT}{F}\ln(c_{(A^-)w}) + \Delta^o_w\varphi^{\theta}_{A^-} + \frac{RT}{F}\ln(\frac{c_{0(dmfc)o}}{2})$$



Square-wave voltammograms representing the redox reaction of dmfc at WE|NB|w three-phase electrode followed by transfer of common inogranic anions across the w|nitrobenzene interface



Peak potentials of the net SW voltammetric responses of dmfc in NB as a function of **the standard potentials of transfer of anions across water | nitrobenzene interface**

$$E_f = E^{\theta}_{dmfc^+/dmfc(o)} - \frac{RT}{F}\ln(a_{(A^-)w}) + \Delta^o_w\varphi^{\theta}_{A^-} + \frac{RT}{F}\ln(\frac{a_{0(dmfc)o}}{2})$$

Applications of the Three-phase electrode for measuring the THERMODYNAMICS of ion transfer at various water|oil phase interfaces

A. water|Nitrobenzene

B. water|*n*-octanol

C. water|Nitrophenyl octyl ether

D. water|D- and L-2-octanol

E. water|D- and L-Menthol

A. Transfer of Ions across the *water*|*nitrobenzene* Interface

- I. ***Inorganic anions***
- **II. *Organic anions-Monoanionic forms of*:**
  - **A. *Phenols***
  - **B. *Cyclo-, Mono, Di-*, and *halogen substituted carboxylic acids***
  - **C. *Amino acids***
  - **D. *Peptides***
  - ***E. Medicaments***

Š. Komorsky-Lovric, K. Riedl, **R. Gulaboski**, V. Mirceski and F. Scholz, *Langmuir* 18 (2002) 8000-8005,

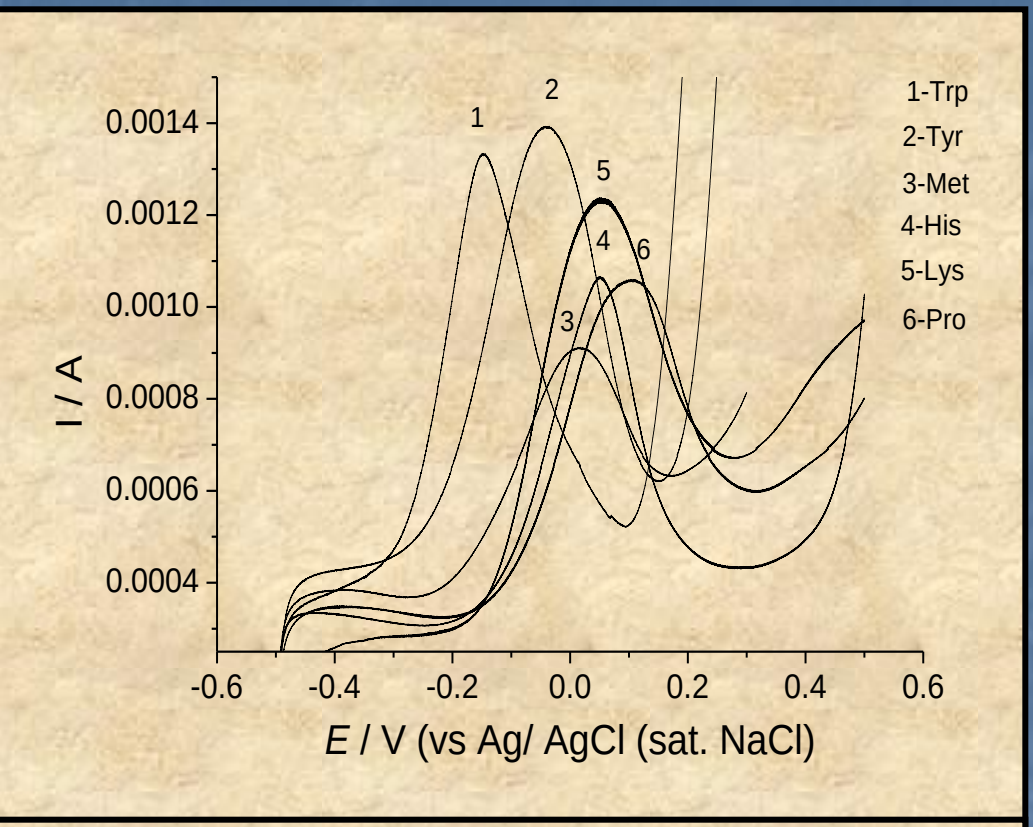
R. Gulaboski, K. Riedl, F. Scholz, *Phys. Chem. Chem. Phys*. 5 (2003) 1284-1289

R. Gulaboski, K. Caban, Z. Stojek, F. Scholz; *Electrochem. Commun*. 6 (2004) 215

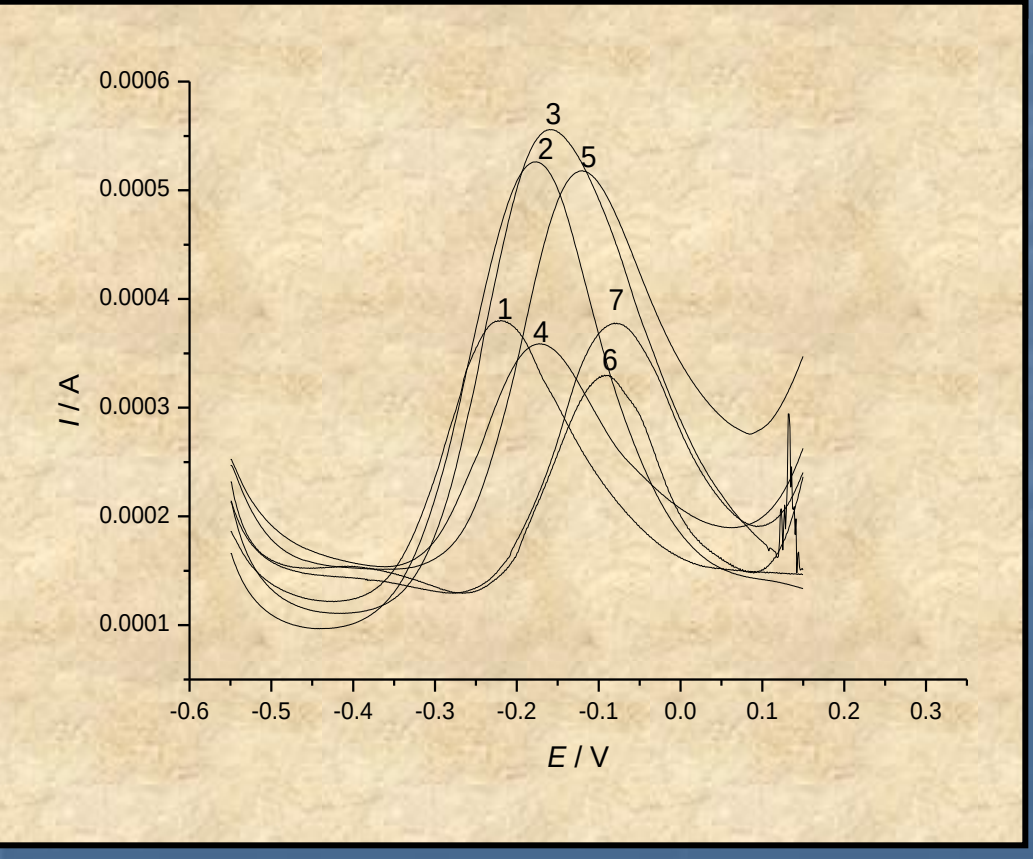
V. Mirceski, **R. Gulaboski**, F. Scholz; *Electrochem. Commun*. 4 (2002) 813-818

V. Mirceski, **R. Gulaboski**, F. Scholz, J. *Electroanal. Chem*. 566 (2004) 351

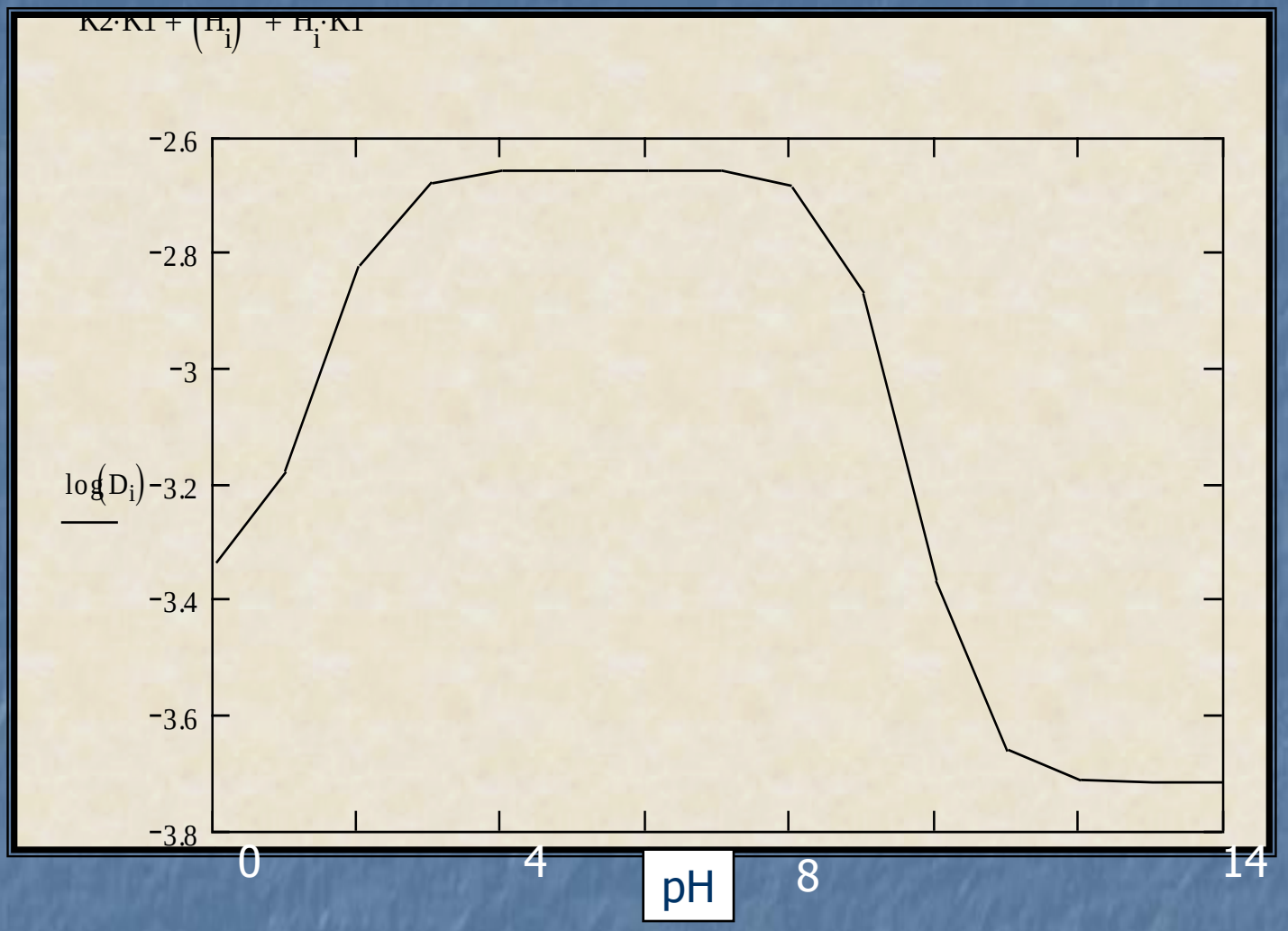
II. B-C. Standard Gibbs energies of transfer of monoanions of various amino acids and peptides



Transfer of monoanions of aminoacids



Transfer of monoanions of some Trp-X peptides



Distribution diagram of Phenyalanine

R. Gulaboski, V. Mirceski, F. Scholz; *Amino Acids* 24 (2003) 149–154

R. Gulaboski, F. Scholz, *J. Phys, Chem. B* 107 (2003) 5650-5657

TRANSFER OF ANIONS ACROSS THE WATER|n-OCTANOL INTERFACE

- among the organic solvents used for studying the lipophilicity of solutes, *n*-OCTANOL is certainly the most important one

- It is an ideal mimic for the biological membranes ***(amphipathic nature similar to those of the lipides in biological membranes,*** long alkyl side chain and OH group)

n-Octanol

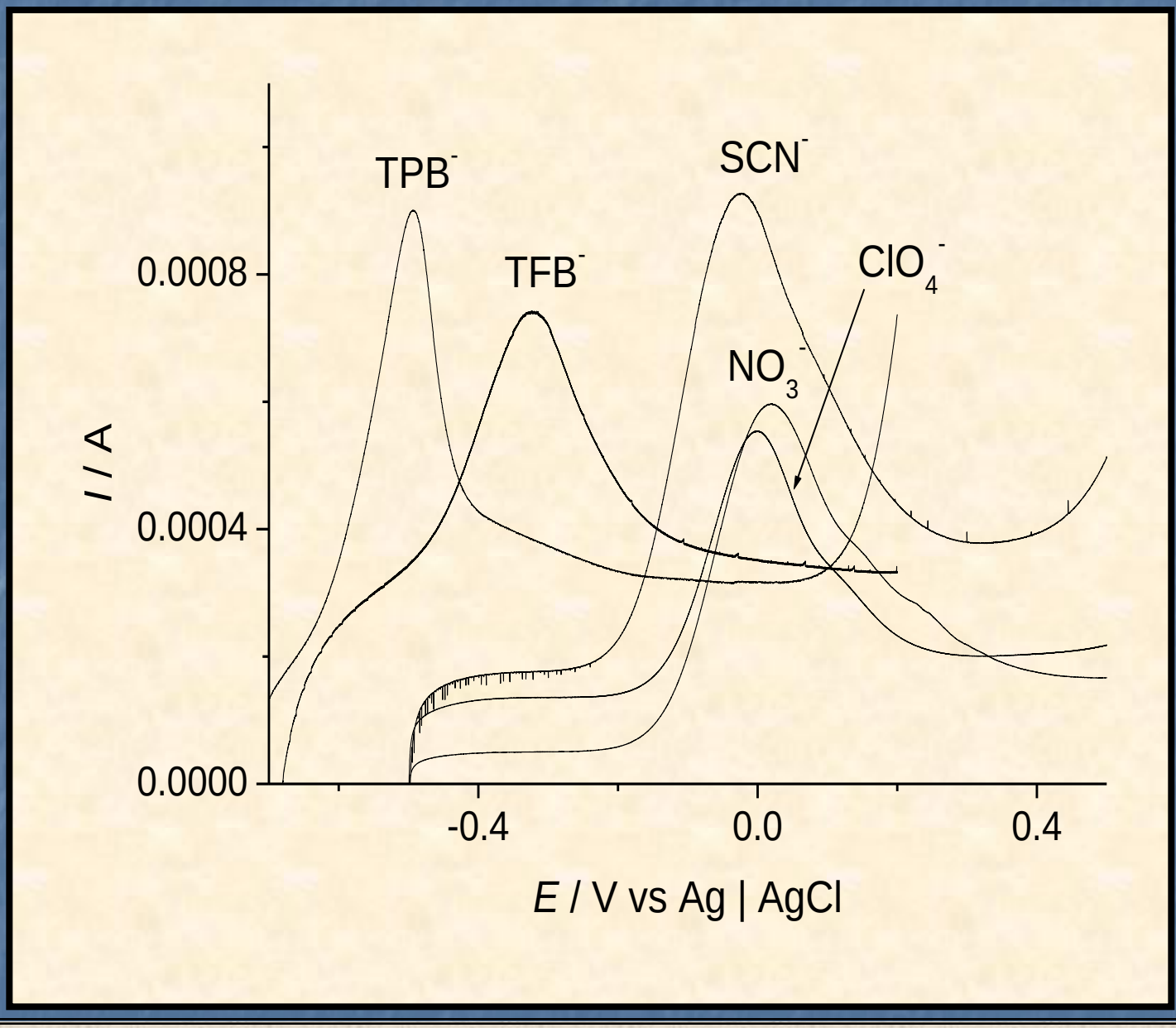
- **No data** in the literature about the standard ***ion potentials*** of transfer across the interface **water|*n*-octanol**:

Reason: ***non-polarizability*** of the interface water|n-Octanol

R. Gulaboski, V. Mirceski, F. Scholz; *Electrochem. Commun.* 4 (2002) 277-283

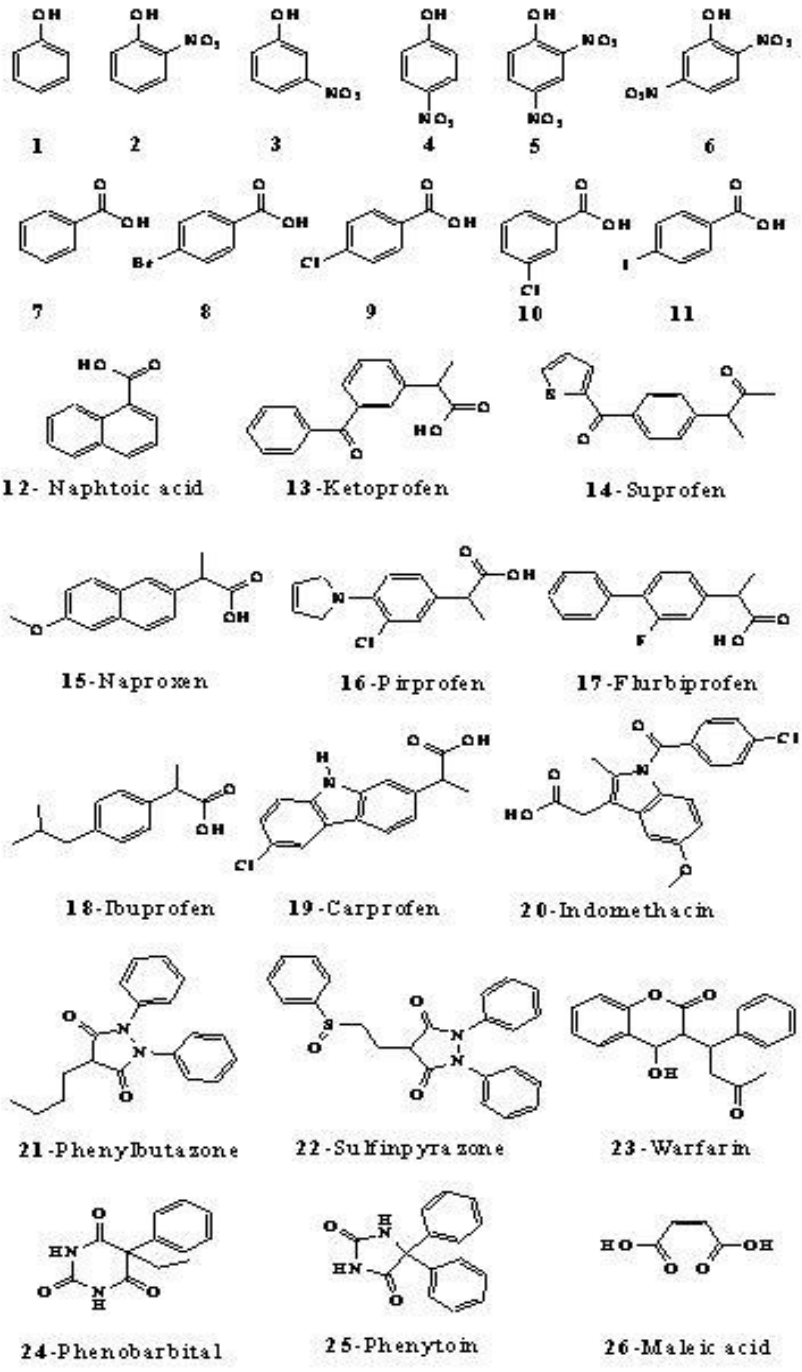
G. Bouchard, A. Galland, P.-A. Carrupt, **R. Gulaboski**, V. Mirceski, F. Scholz, H. H. Girault, *Phys. Chem. Chem. Phys.* 5 (2003) 3748-3751

$$dmfc(n\text{-}oct) + A^-(w) \Leftrightarrow dmfc^+(n\text{-}oct) + A^-(n\text{-}oct) + 1e^-$$



Transfer of some common anions across water|***n*-octanol** interface

Transfer of anions of medicaments and model compounds across w|n-octanol interface

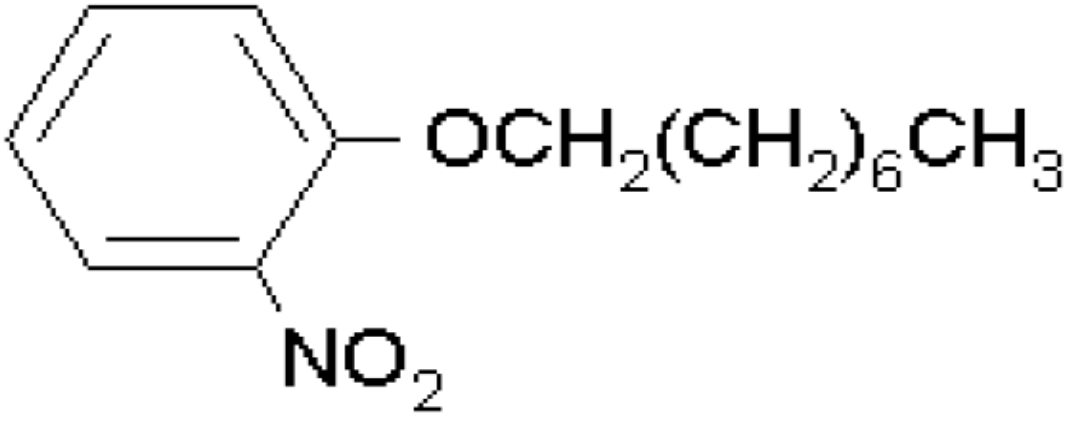


G. Bouchard, A. Galland, P.-A. Carrupt, B. Testa, R. Gulaboski, V. Mirčeski, F. Scholz, H. H. Girault

Comparison of solvation properties of Nitrophenyl octyl ether, Nitrobenzene, and n-Octanol

2-Nitrophenyl octyl ether-used as an alternative solvent for *n*-octanol

It *shares* the structures of Nitrobenzene and *n*-octanol



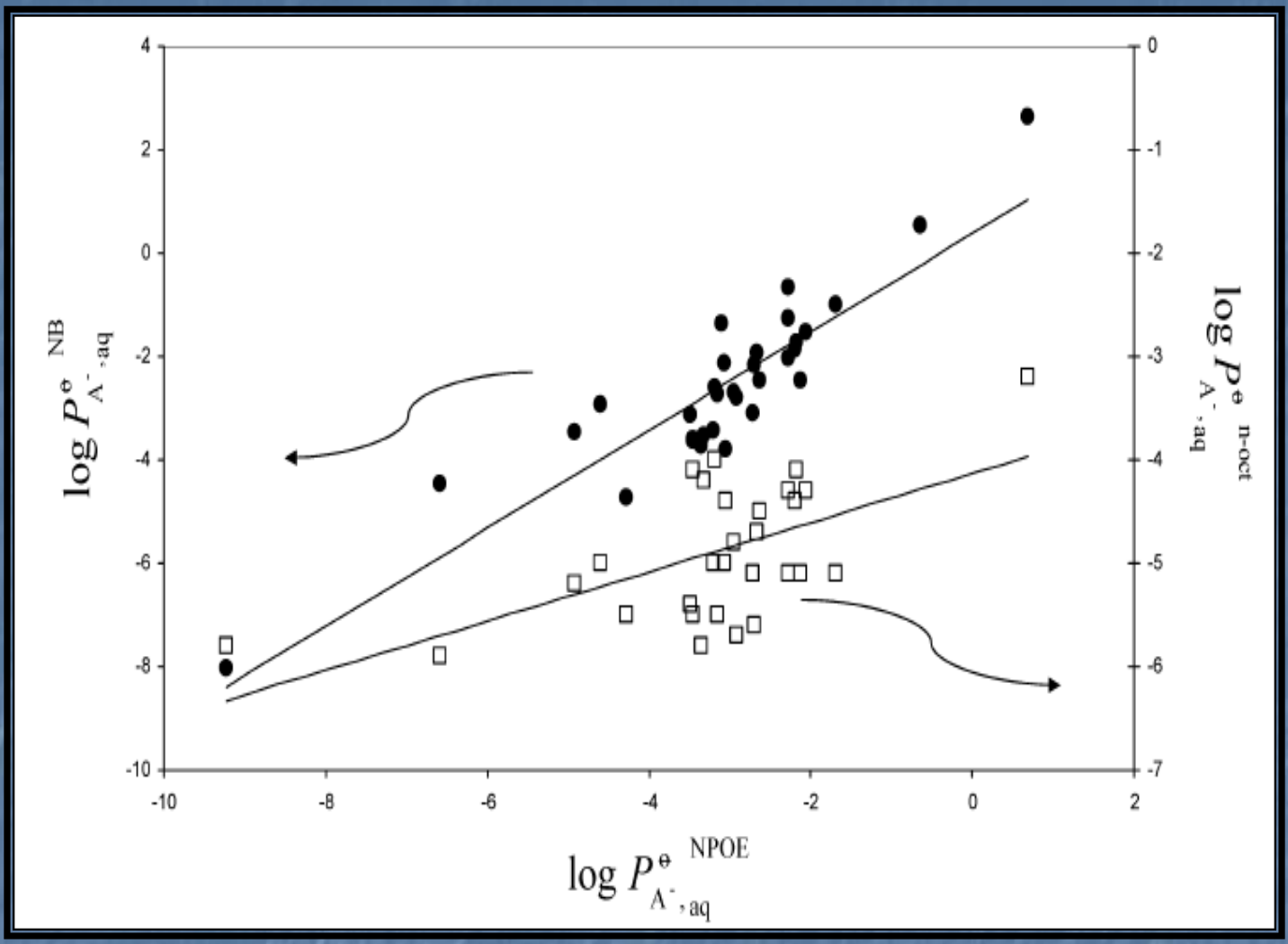
2-Nitrophenyl octyl ether

11. **R. Gulaboski**, A. Galland, G. Bouchard, K. Caban, A. Kretschmer, P.-A. Carrupt, Z. Stojek, H. H. Girault, F. Scholz, *J. Phys. Chem. B*, 108 (2004) 4565

Table 2 Standard Gibbs energies of transfer and partition coefficients of the studied anions.

n°	Compound	$\Delta G_{tr,A}^{0,w\rightarrow NB}$ a)	$\Delta G_{tr,A}^{0,w\rightarrow NPOE}$ a)	$\Delta G_{tr,A}^{0,w\rightarrow OCT}$ a)b)	log $P_{NB}^{0,A}$	log $P_{NPOE}^{0,A}$	log $P_{OCT}^{0,A}$ b)	r (Å)c)
1	Phenol	20.45	19.50	23.13	-3.62	-3.46	-4.10	2.78
2	2-Nitrophenol	14.60	18.00	22.56	-2.59	-3.19	-4.00	2.98
3	3-Nitrophenol	20.00	18.75	23.70	-3.54	-3.32	-4.20	2.98
4	4-Nitrophenol	21.48	17.20	24.82	-3.81	-3.05	-4.40	2.98
5	2,4-Dinitrophenol	8.70	11.62	24.25	-1.54	-2.06	-4.30	3.15
6	2,5-Dinitrophenol	14.00	14.85	25.40	-2.48	-2.63	-4.50	3.15
7	Benzoic acid	21.00	18.95	32.72	-3.72	-3.36	-5.80	2.97
8	4-Bromobenzoic acid	12.00	17.32	28.20	-2.13	-3.07	-5.00	3.15
9	4-Chlorobenzoic acid	12.25	15.23	31.59	-2.17	-2.70	-5.60	3.09
10	3-Chlorobenzoic acid	15.25	16.65	27.08	-2.70	-2.95	-4.80	3.09
11	4-Iodobenzoic acid	14.00	12.00	28.77	-2.48	-2.13	-5.10	3.21
12	Naphtoic acid	15.50	17.80	31.05	-2.74	-3.15	-5.50	3.77
13	Ketoprofen	19.33	18.05	28.20	-3.42	-3.20	-5.00	3.84
14	Suprofen	15.80	16.47	32.15	-2.80	-2.92	-5.70	3.79
15	Naproxen	11.50	12.86	28.77	-2.04	-2.28	-5.10	3.70
16	Pirprofen	5.65	9.55	28.75	-1.00	-1.69	-5.10	3.76
17	Flurbiprofen	10.50	12.35	24.80	-1.86	-2.19	-4.40	3.75
18	Ibuprofen	17.40	15.34	28.77	-3.08	-2.72	-5.10	3.59
19	Carprofen	-14.80	-3.85	18.05	2.62	0.68	-3.20	3.82
20	Indomethacin	11.00	15.05	26.50	-1.95	-2.67	-4.70	4.06
21	Phenylbutazone	3.70	12.85	24.25	-0.65	-2.28	-4.30	4.13
22	Sulfinpyrazone	7.10	12.85	24.25	-1.26	-2.28	-4.30	4.40
23	Warfarine	9.80	12.30	23.13	-1.74	-2.18	-4.10	4.05
24	Phenobarbital	26.75	24.10	31.02	-4.74	-4.27	-5.50	3.64
25	Phenytoine	17.70	19.65	30.45	-3.14	-3.48	-5.40	3.78
26	Maleic acid	20.30	19.50	31.02	-3.60	-3.46	-5.50	2.75
27	Picric acid	-3.00	3.65	n.m.d)	0.53	-0.65	n.m.b)	3.28

a) in kJ.mol^{-1} b) taken from reference [35] c) van der Waals radius of the ion, d) non measured



Comparison between partition coefficients in w|NB and w|NPOE, and w|*n*-oct and w|NPOE

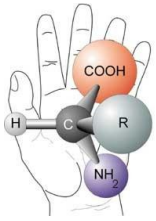
F. Scholz, **R. Gulaboski**, *ChemPhysChem* 2005, 6, 16–28 (**Review**)

3. Quantification of the enantiomeric anion transfer energies across water|chiral liquid interface

graphite electrode

e^-

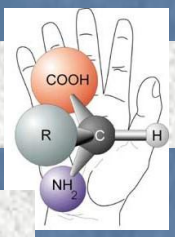
chiral solvent



dmfc ⇄ dmfc$^+$

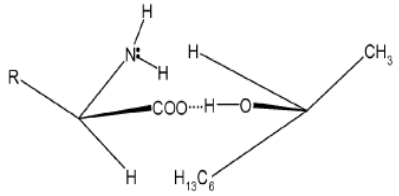
chiral$^-_{(org)}$

chiral$^-_{(aq)}$

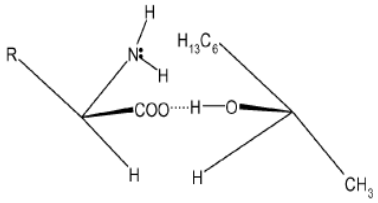


aqueous electrolyte
(Cat$^+$, chiral$^-$)

(Racemic mixtures can be separated)

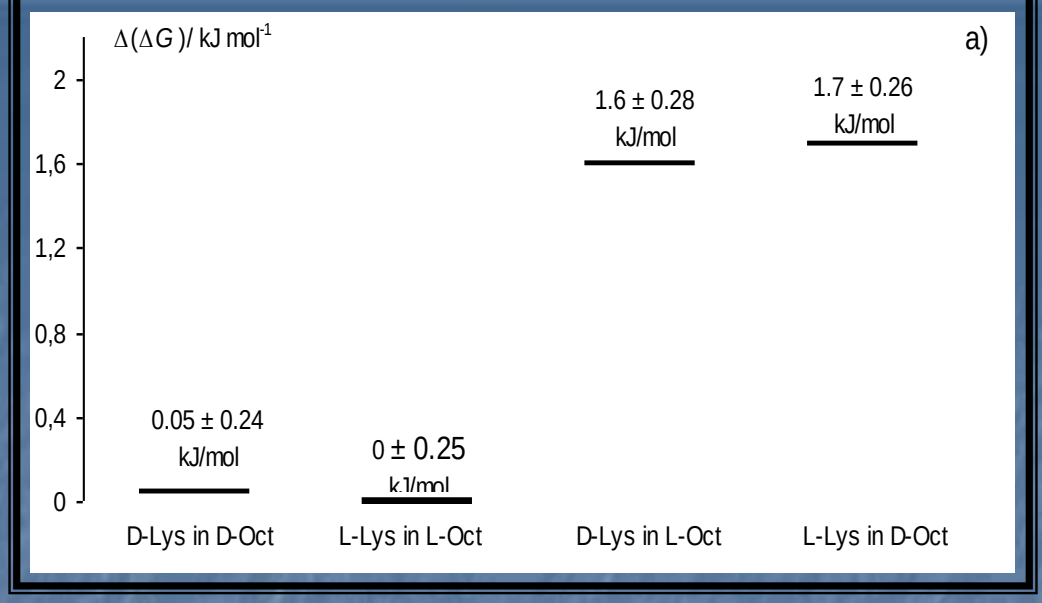


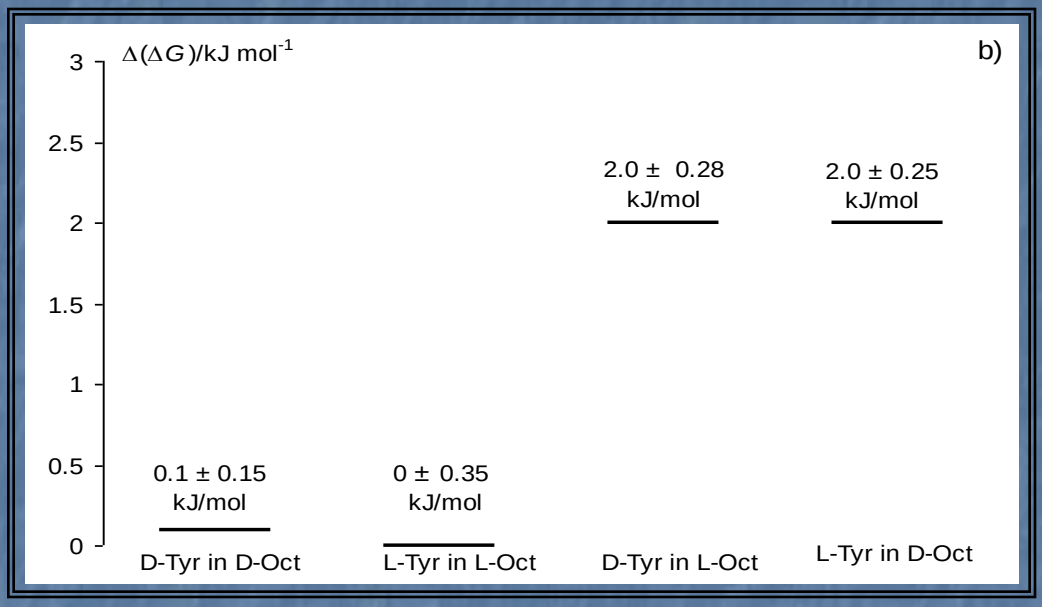
D-ion/D-solvent

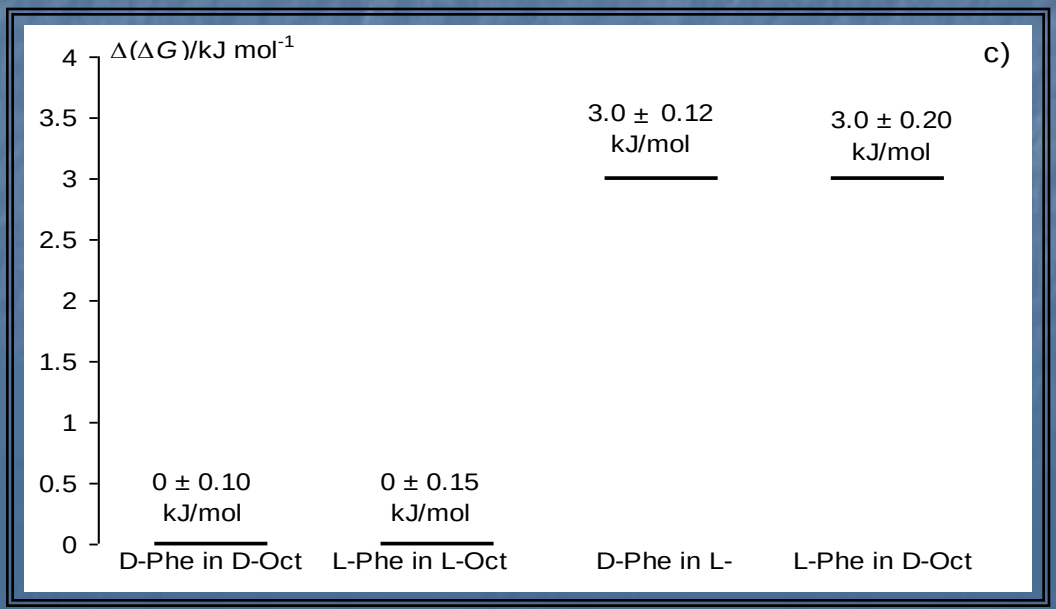


D-ion/L-solvent

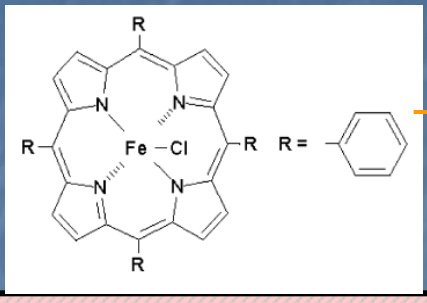
F. Scholz, **R. Gulaboski**, *Faraday Discuss.*, 2005, 129, 169–177
F. Scholz, **R. Gulaboski**, V. Mirceski, P. Langer; *Electrochem. Commun.* 4 (2002) 659-662


a)
Δ(ΔG)/ kJ mol-1
2
1,6
1,2
0,8
0,4
0
0.05 ± 0.24 kJ/mol
0 ± 0.25 kJ/mol
1.6 ± 0.28 kJ/mol
1.7 ± 0.26 kJ/mol
D-Lys in D-Oct
L-Lys in L-Oct
D-Lys in L-Oct
L-Lys in D-Oct


b)
Δ(ΔG)/kJ mol-1
3
2.5
2
1.5
1
0.5
0
0.1 ± 0.15 kJ/mol
0 ± 0.35 kJ/mol
2.0 ± 0.28 kJ/mol
2.0 ± 0.25 kJ/mol
D-Tyr in D-Oct
L-Tyr in L-Oct
D-Tyr in L-Oct
L-Tyr in D-Oct


c)
Δ(ΔG)/kJ mol-1
4
3.5
3
2.5
2
1.5
1
0.5
0
0 ± 0.10 kJ/mol
0 ± 0.15 kJ/mol
3.0 ± 0.12 kJ/mol
3.0 ± 0.20 kJ/mol
D-Phe in D-Oct
L-Phe in L-Oct
D-Phe in L-
L-Phe in D-Oct

Transfer of cations across the water|Nitrobenzene interface



Fe(III)TPhP

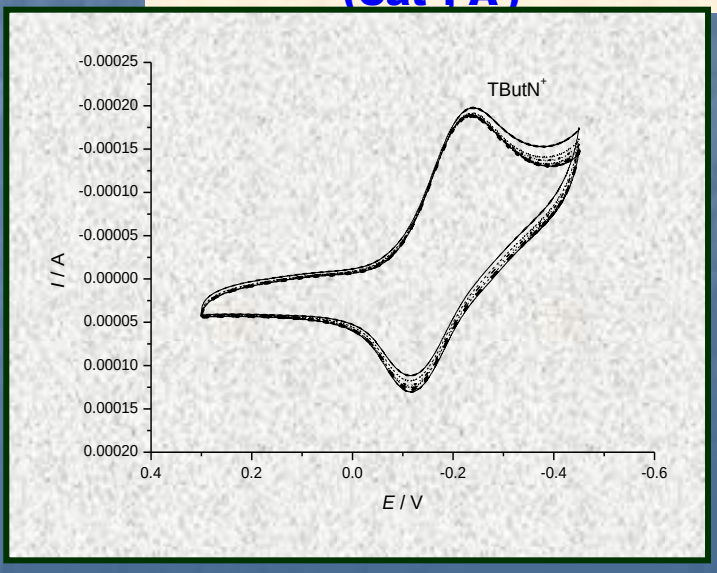
graphite electrode

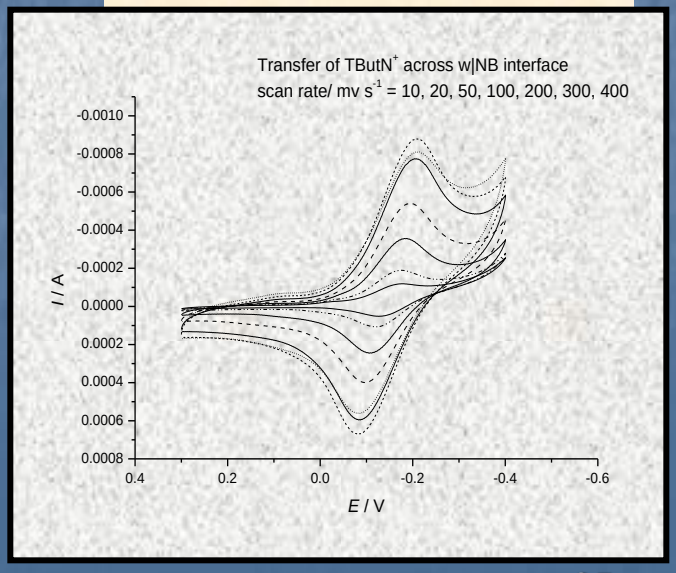
NB **Fe(III)TPhP +e-** ⇄ **Fe(II)TPhP$^-$**

Cat$^+$ ⇄

aqueous electrolyte **(Cat$^+$, A$^-$)**

Cat$^+$ **(aq)**





F. Scholz, **R. Gulaboski**, K. Caban, *Electrochem. Commun.* 5 (2003) 929

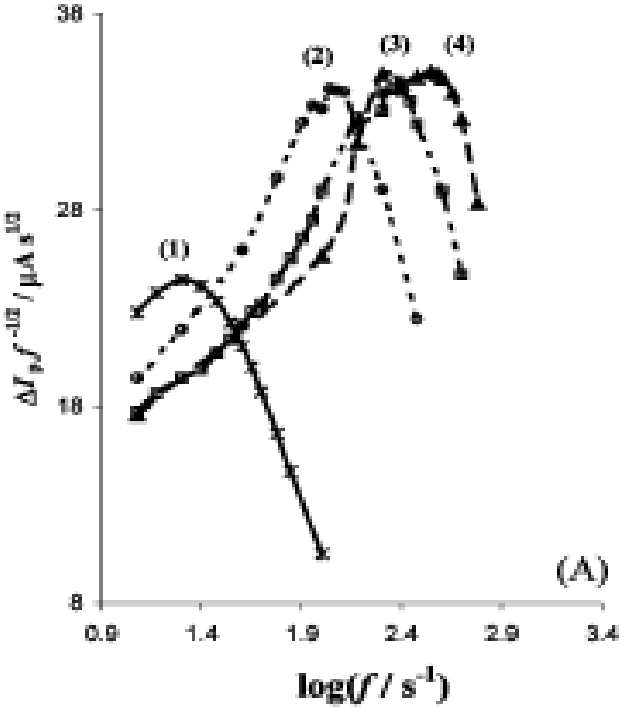
EXPLORING THE THREE-PHASE ELECTRODE FOR MEASURING ***THE KINETICS*** OF ION TRANSFER ACROSS L|L INTERFACE

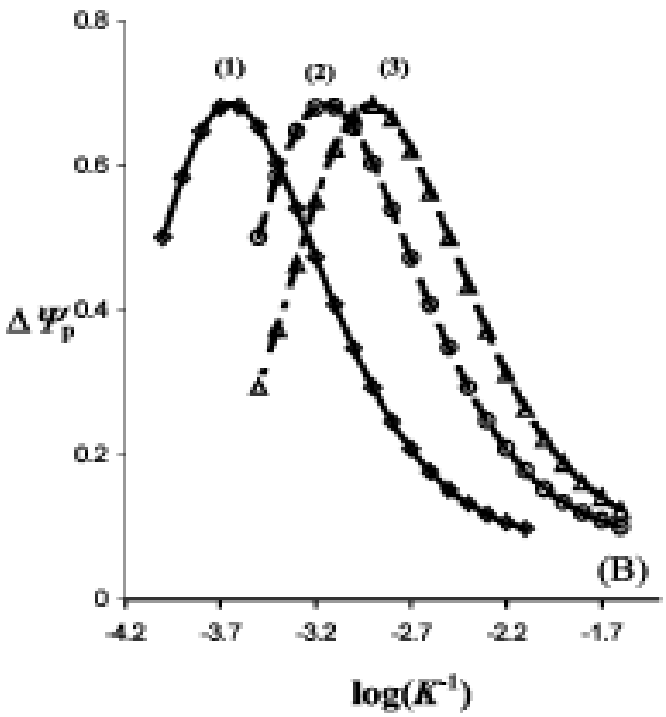
Considering theoretically the reaction occuring at the Three-Phase Electrode:

$$Ox_{(nb)} + X^-_{(nb)} + e \rightleftharpoons Red^-_{(nb)} + X^-_{(w)}$$

the ***apparent reversibility*** depends on dimensionless kinetic parameter

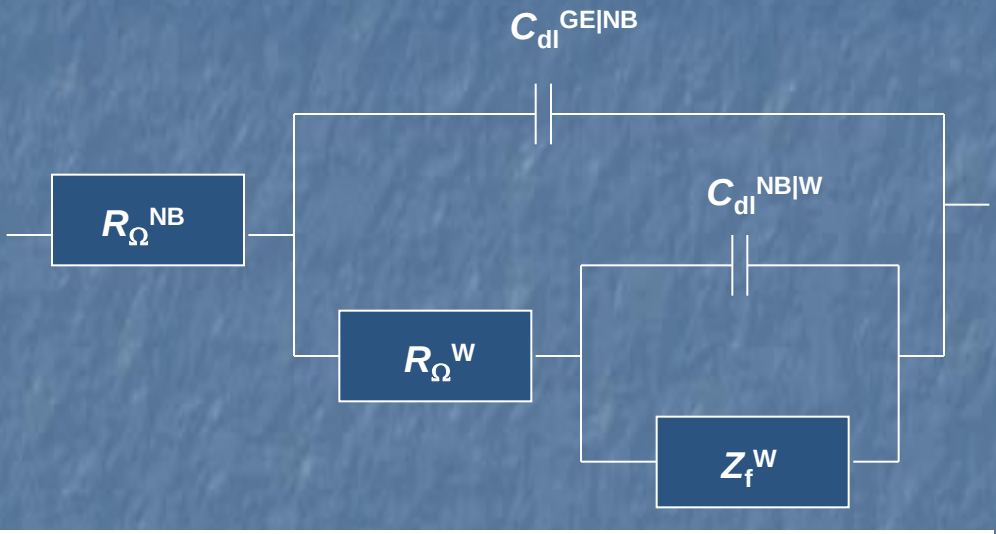
$$K' = \frac{k'_s c^*_{X^-_{(w)}} \exp(\beta \ln(c^*_{X^-_{(nb)}} / c^*_{X^-_{(w)}}))}{\sqrt{Df}}$$

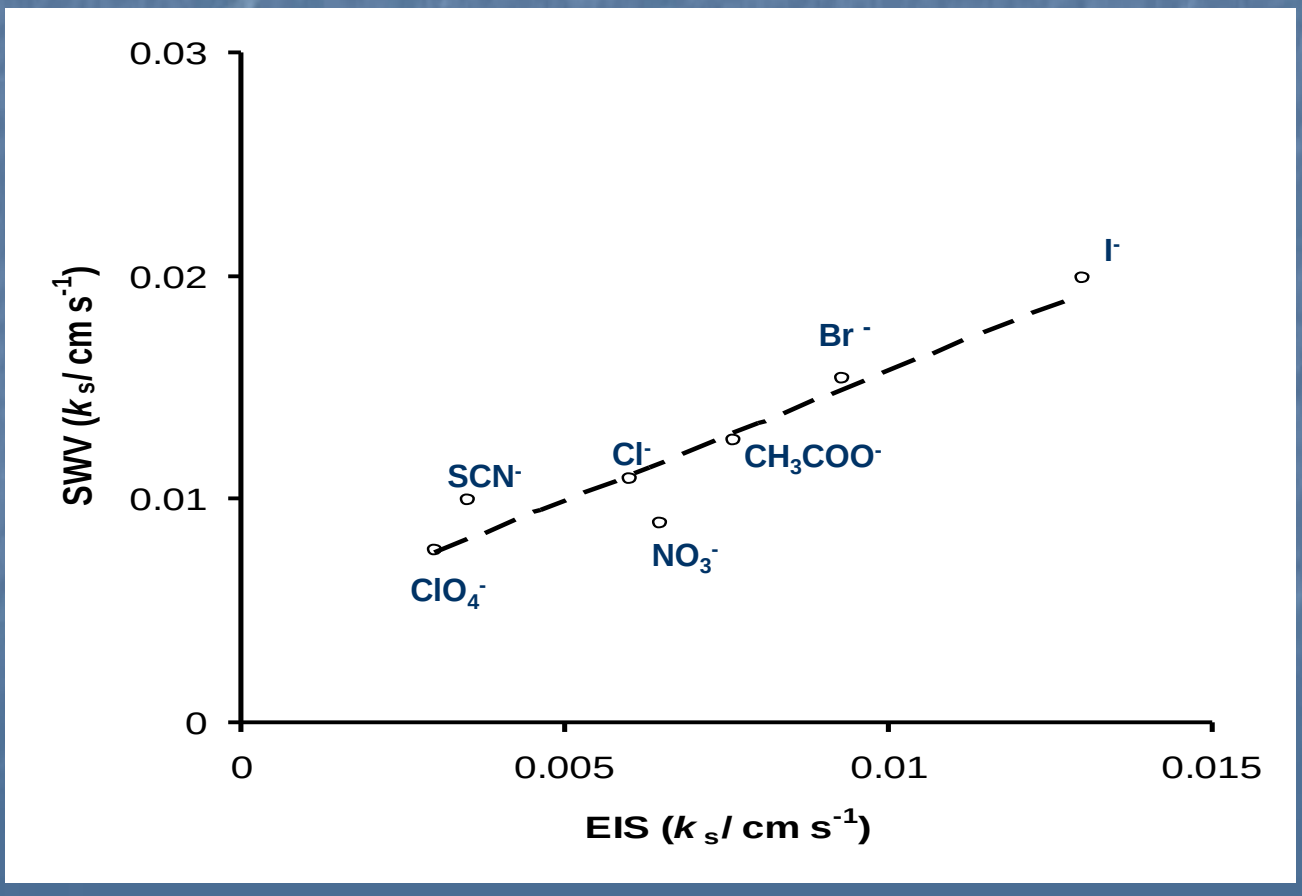




Experimental (A) and theoretical (B) quasireversible maxima for the reaction of anion transfer at Three-phase electrode

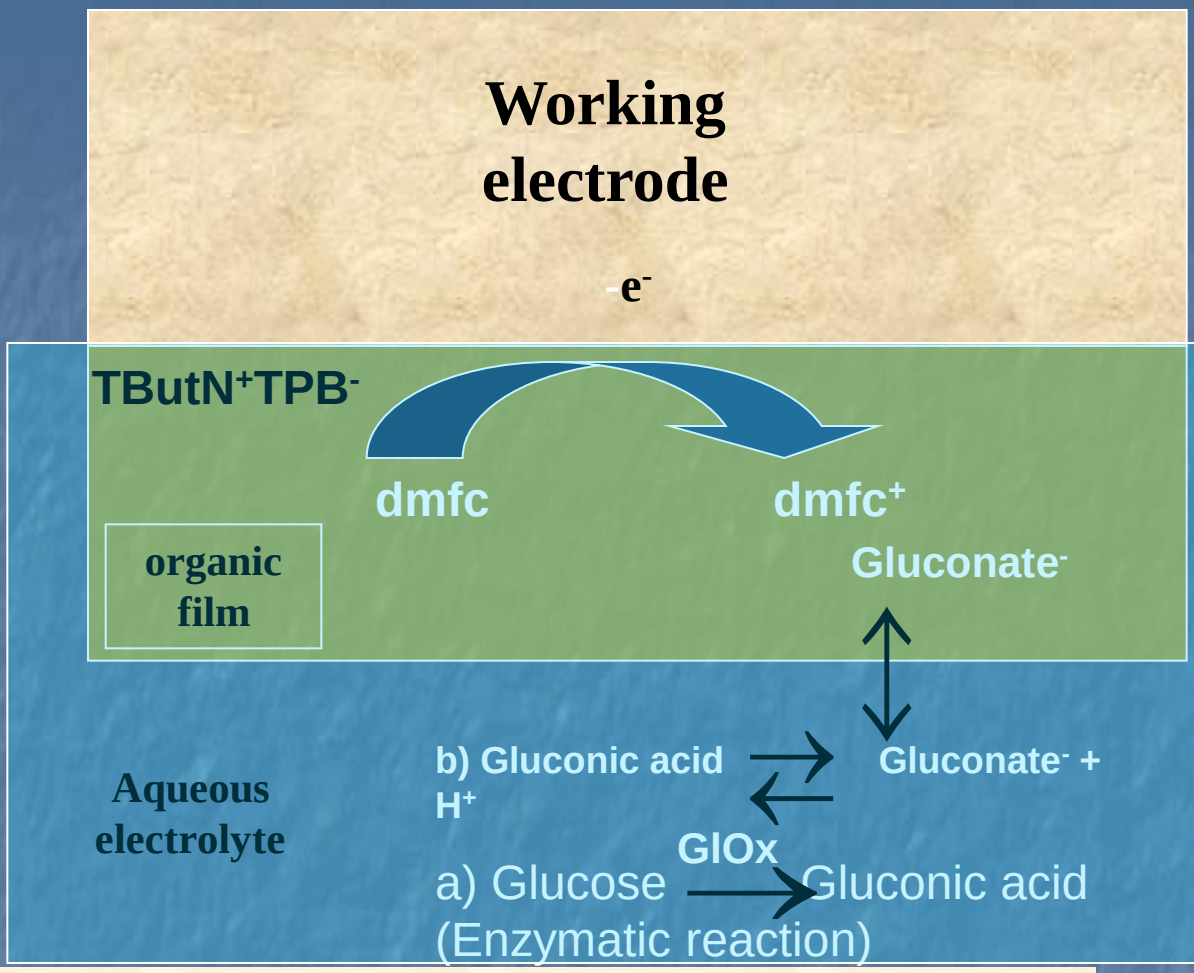
Kinetics of Ion Transfer measured by Electrochemical Impedance Spectroscopy (EIS)

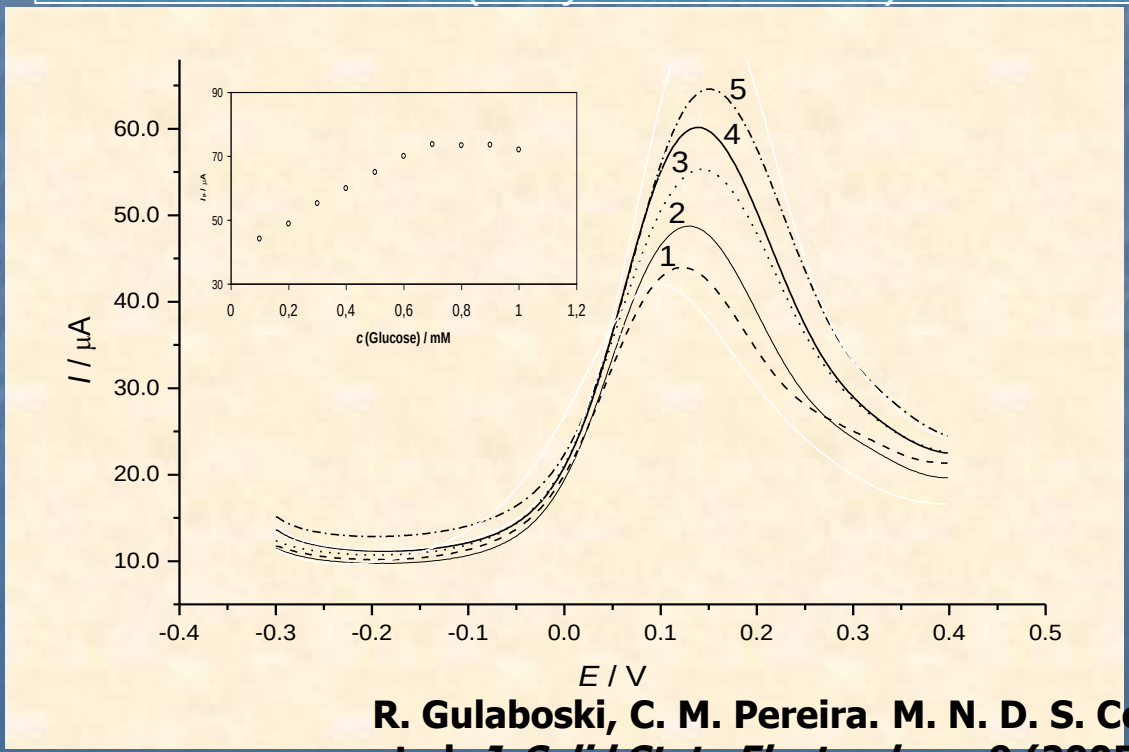




R. Gulaboski, V. Mirceski, C. M. Pereira.
M. N. D. S. Cordeiro et al. *Langmuir* (submitted)

Three-phase electrode-as a tool for making bio-sensors

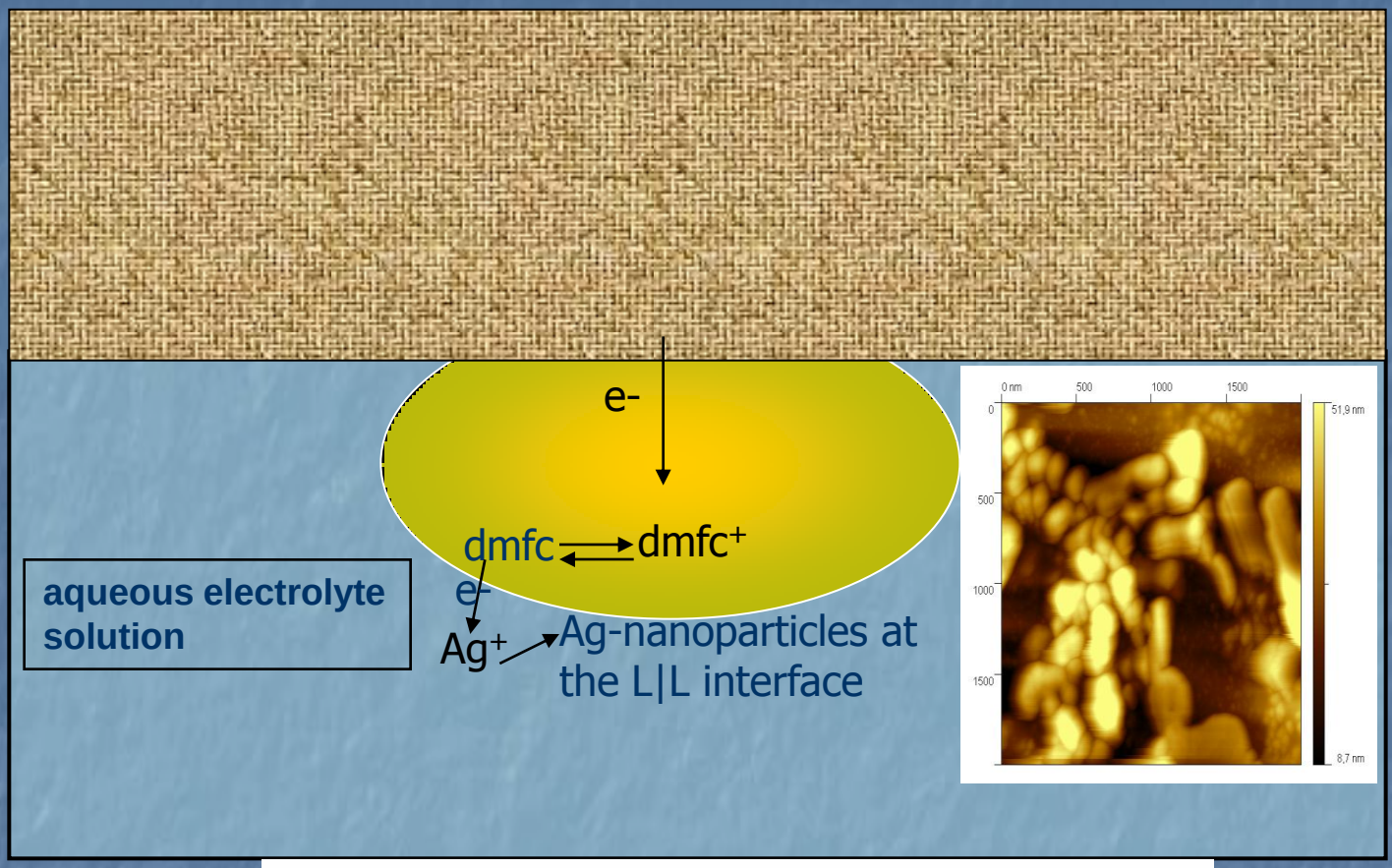


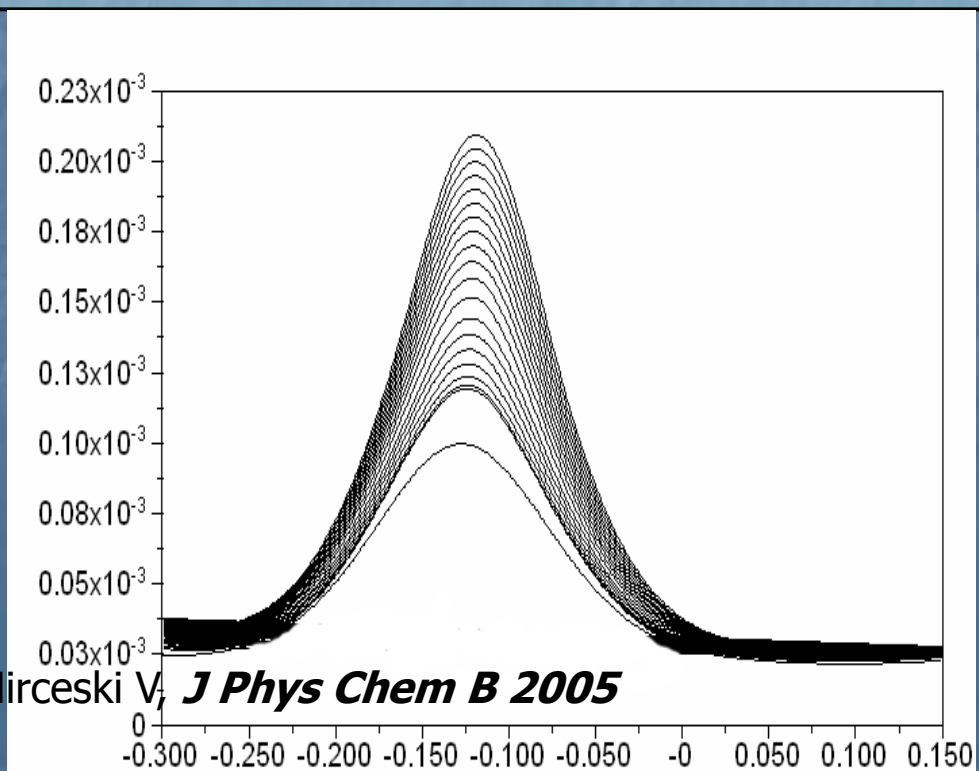


R. Gulaboski, C. M. Pereira. M. N. D. S. Cordeiro, et al. *J. Solid State Electrochem.* 9 (2005) 469-474

R. Gulaboski, C. M. Pereira. M. N. D. S. Cordeiro, et al., *J. Phys. Chem B* 109 (2005) 12549

Ag-nanoparticles Synthezis at Three-Phase Electrode





Gulaboski R, Mirceski V, ***J Phys Chem B 2005***

Which effects affect the lipophilicity of ions?

Energy of solvation=

Energy of making a cavity in the solvent to accomodate the solute

Energy of reorganization of solvent molecules

Short-term interactions
(H-bonds, van der Walls interactions, electrostatic interactions)

First model of ion-solvent interaction:

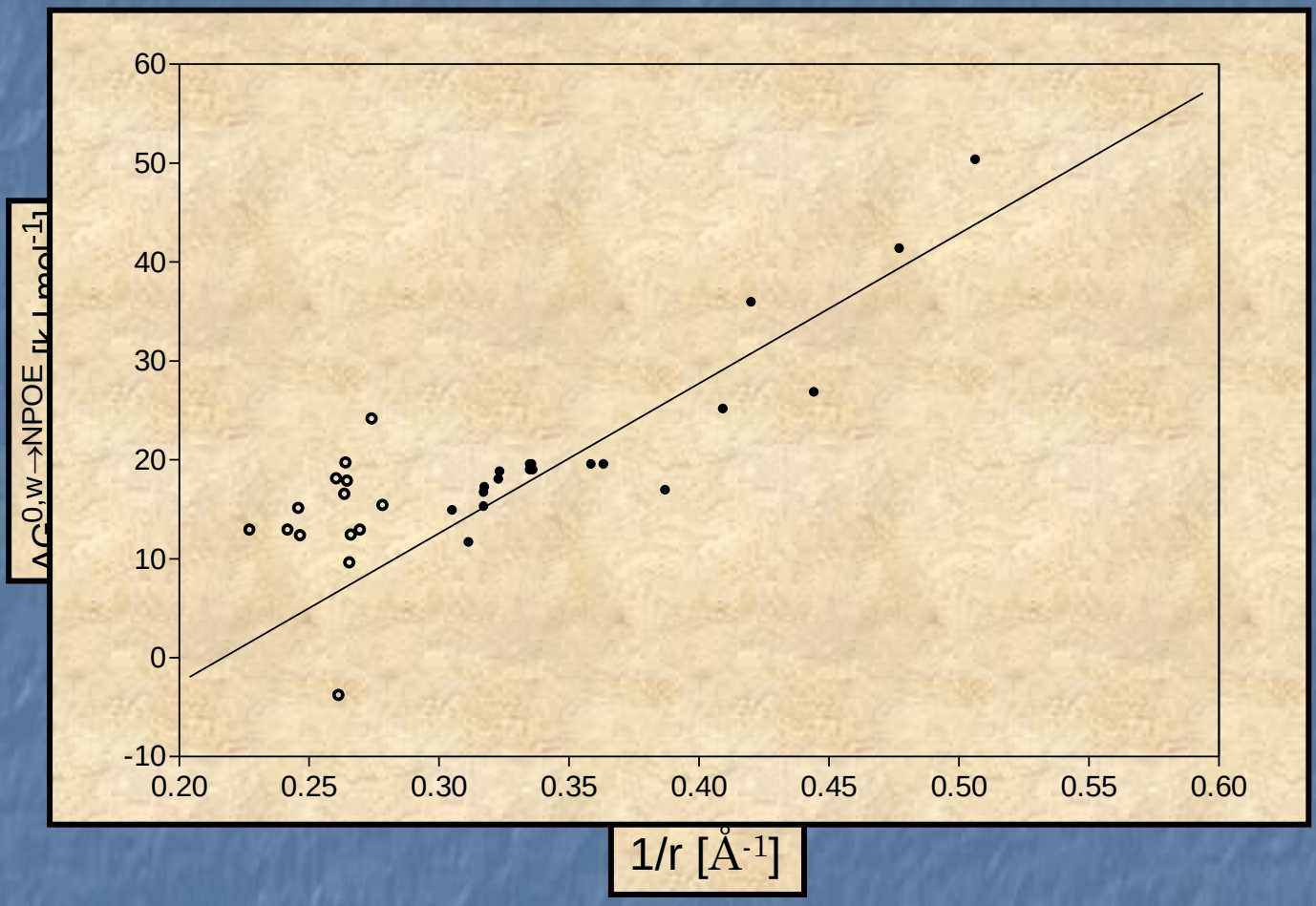
Born electrostatic theory:

$$\Delta_w^{uc} G^{\theta}_{Born} = -\frac{N_A z^2 e^2}{8\pi\varepsilon_0 r}\left(\frac{1}{\varepsilon_{(w)}} - \frac{1}{\varepsilon_{(o)}}\right)$$

Major weaknesses:

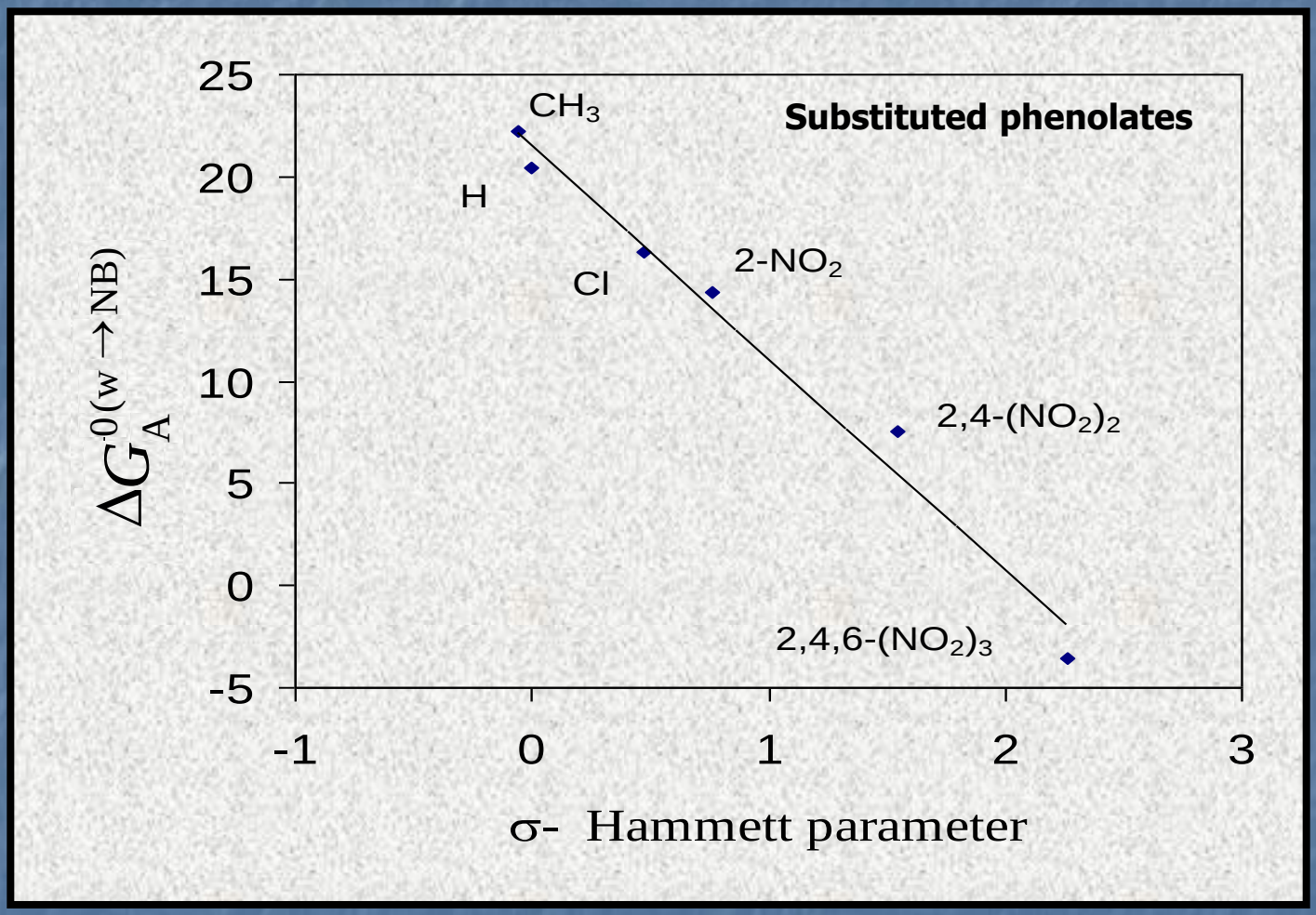
Neglects the charge delocalization effects

Neglects the energy of cavity formation


60
50
40
30
20
10
0
-10
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
1/r [Å-1]

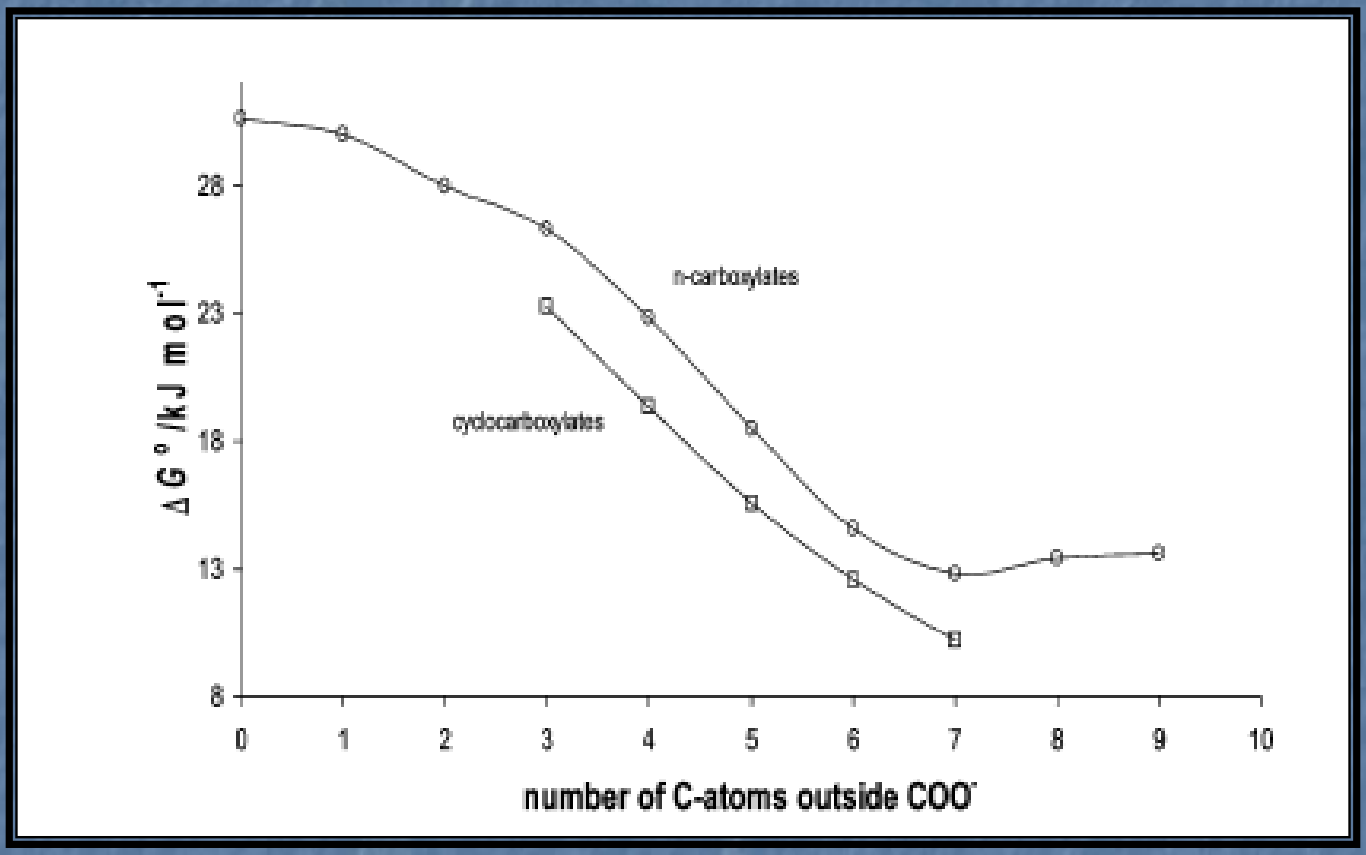
Influence of the charge delocalization effects to the lipophilicity of ions

For anions-presence of the groups with **negative inductive effect** {**NO_2, X, OH**} will produce **dispersion** of the negative charge throughout the structure of dissolved anions



Influence of the energy of making a cavity to the lipophilicity of the ions

$$E_{cav.} = 4\sigma_w^{o} A_i N_A$$



***Summary*:**

Ion transfer processes studied by ***three-phase electrodes:***

-common three-electrode setup
-simple, precise and fast determinations of *thermodynamic and kinetic parameters*
-the approach applicable to different organic solvents (octanol(s), menthol, nitrobenzene, dichlorethan, nitrophenyl octyl ether, …)
-a huge data base of new determined standard Gibbs energies of transfer of various ions as well as of k_s values
-Potential applications as a sensor and by the ion separation processes
-MD Simulations needed for molecular understanding (N. Cordeiro, J. Miguel)

Acknowledgments

➢I thank **Prof. Natalia Cordeiro** and **Prof. Carlos Pereira** from **Porto University**

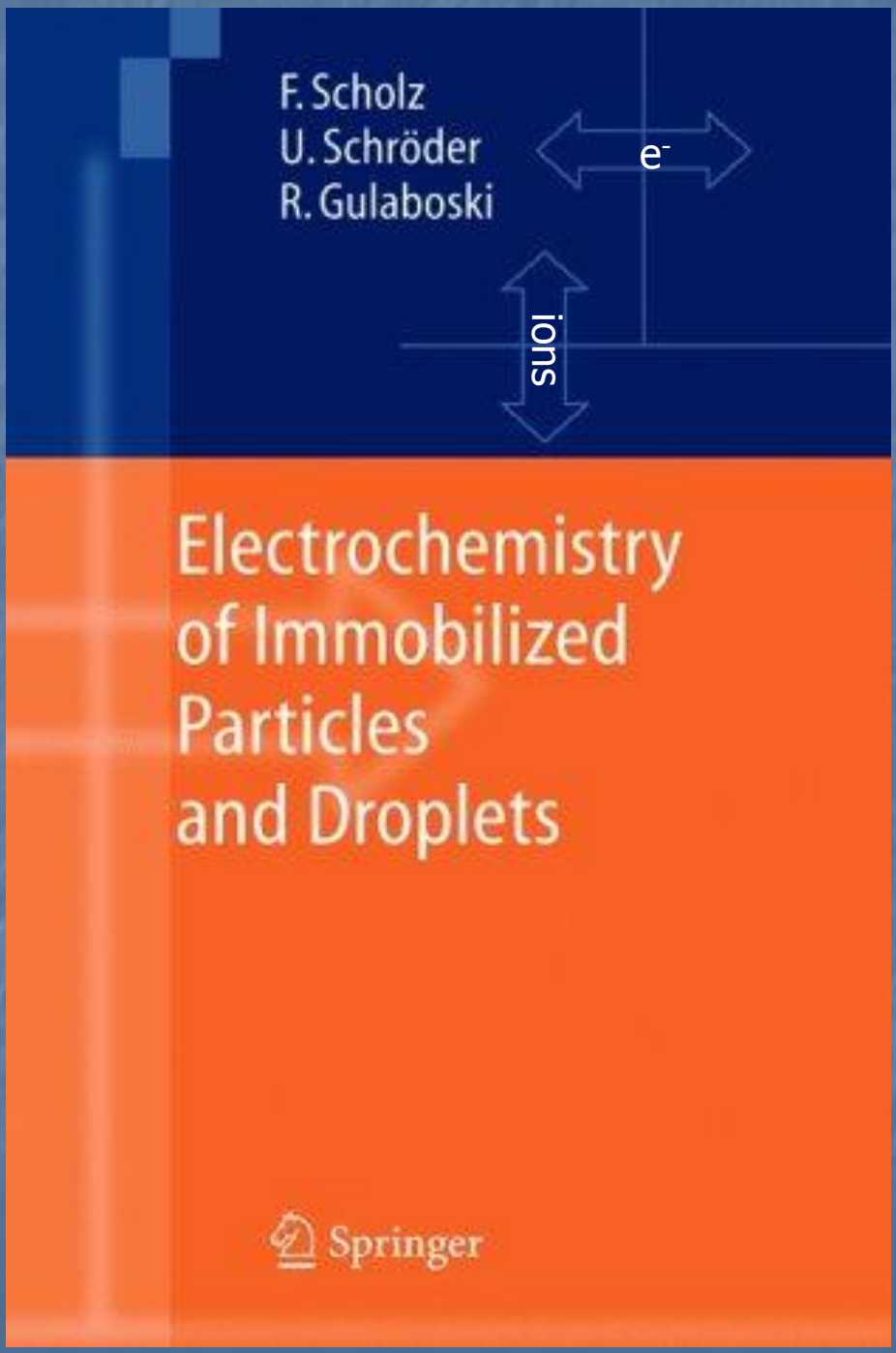
➢I thank my supervisor **Prof. Fritz Scholz** from Greifswald-University, Germany.

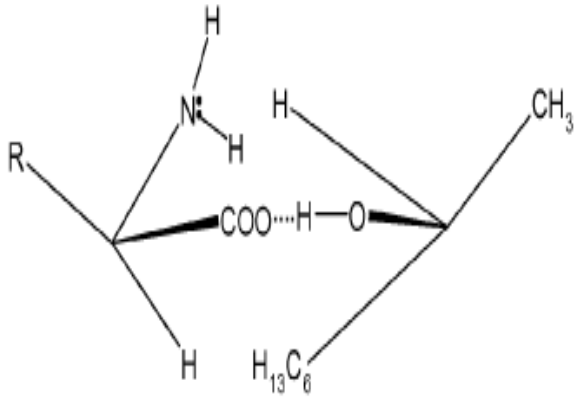
➢I thank my former Macedonian supervisor **Doc. Dr Valentin Mirčeski, Skopje University, MACEDONIA.**

➢I thank **Prof. Šebojka Komorsky-Lovrić** and **Prof. Milivoj Lovrić , Zagreb, Croatia.**

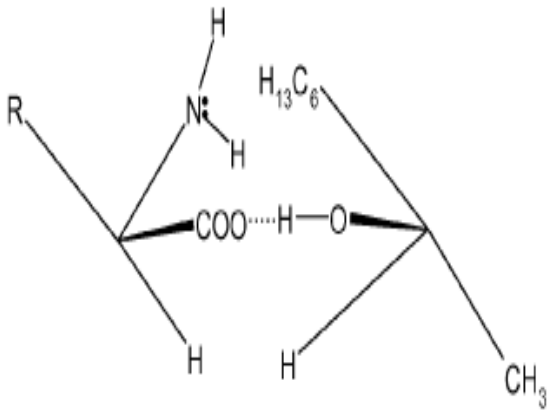
➢I thank **Dr. Jorge Miguel** and **Prof A. F. Silva, M. Chirea**

15. **Electrochemistry of Immobilized Particles and Droplets**-F. Scholz, U. Schröder, **R. Gulaboski**, Springer, Heidelberg, Berlin 2005.





D-ion/D-solvent



D-ion/L-solvent

Limitations of the 4-electrode voltammetry at ITIES:

- **Narrow potential windows**
- **Applicable to few organic solvents only, mainly to 1,2 dichlorethan and Nitrobenzene**

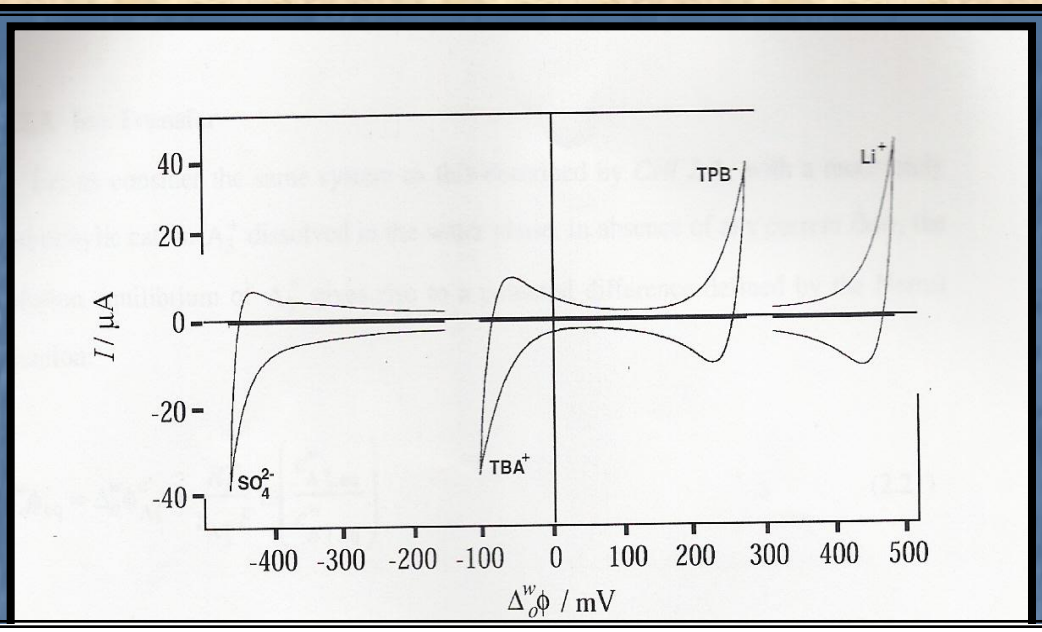
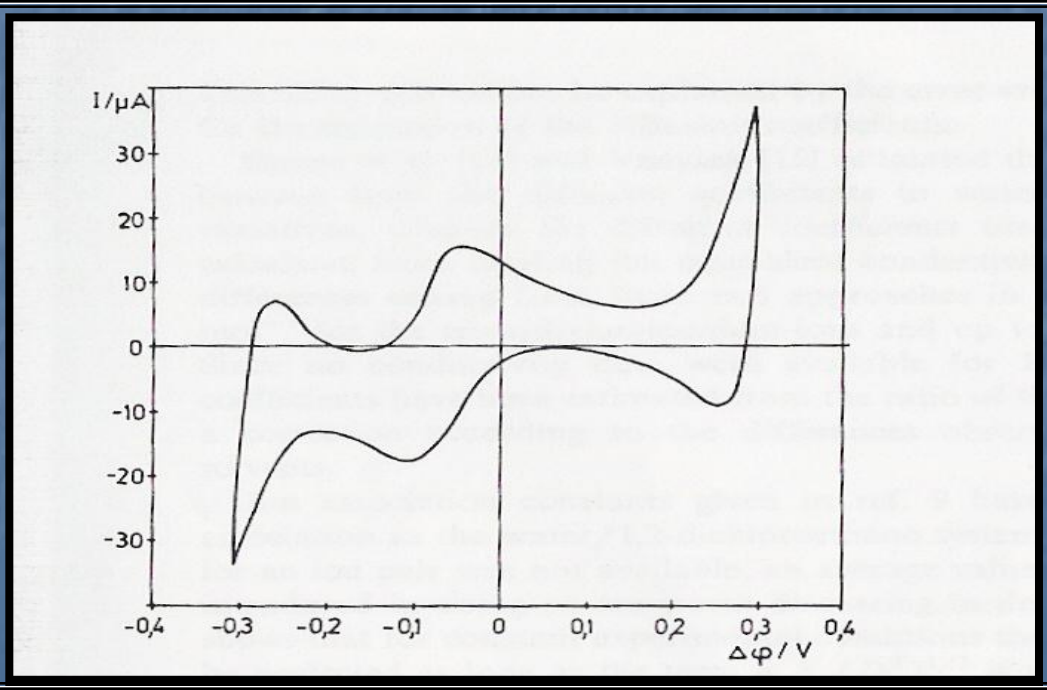


Figure: blank voltammograms obtained by four-electrode measurements

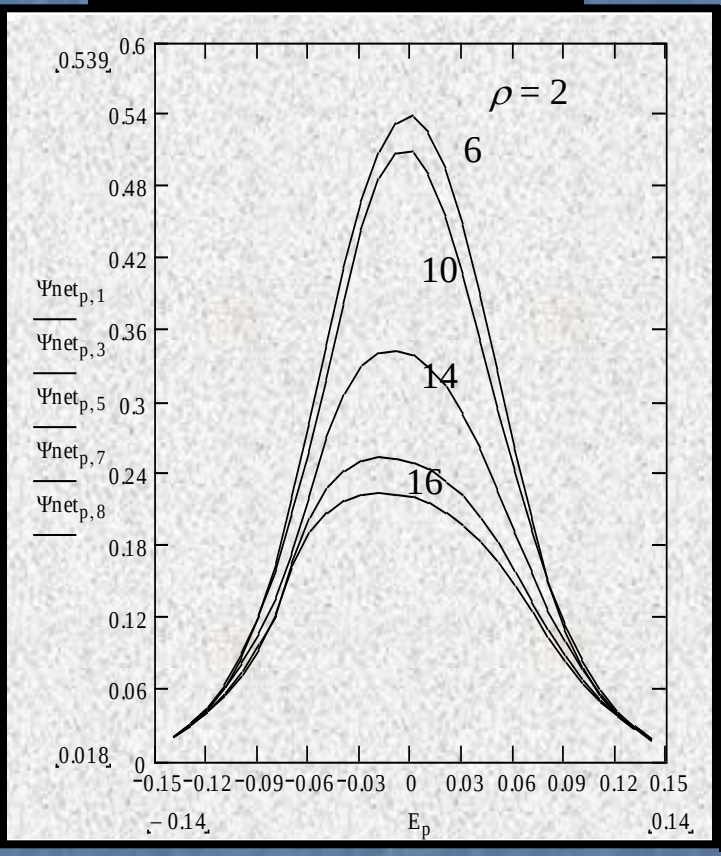


Transfer of perchlorate across water/NB interface

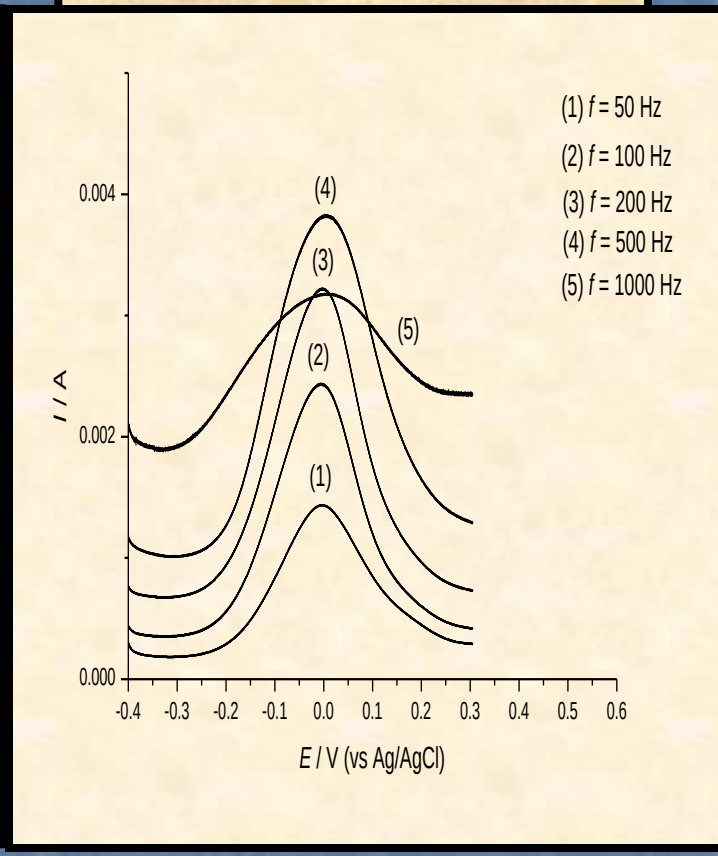
Influence of the uncompensated resistance in the square-wave thin-film voltammetry

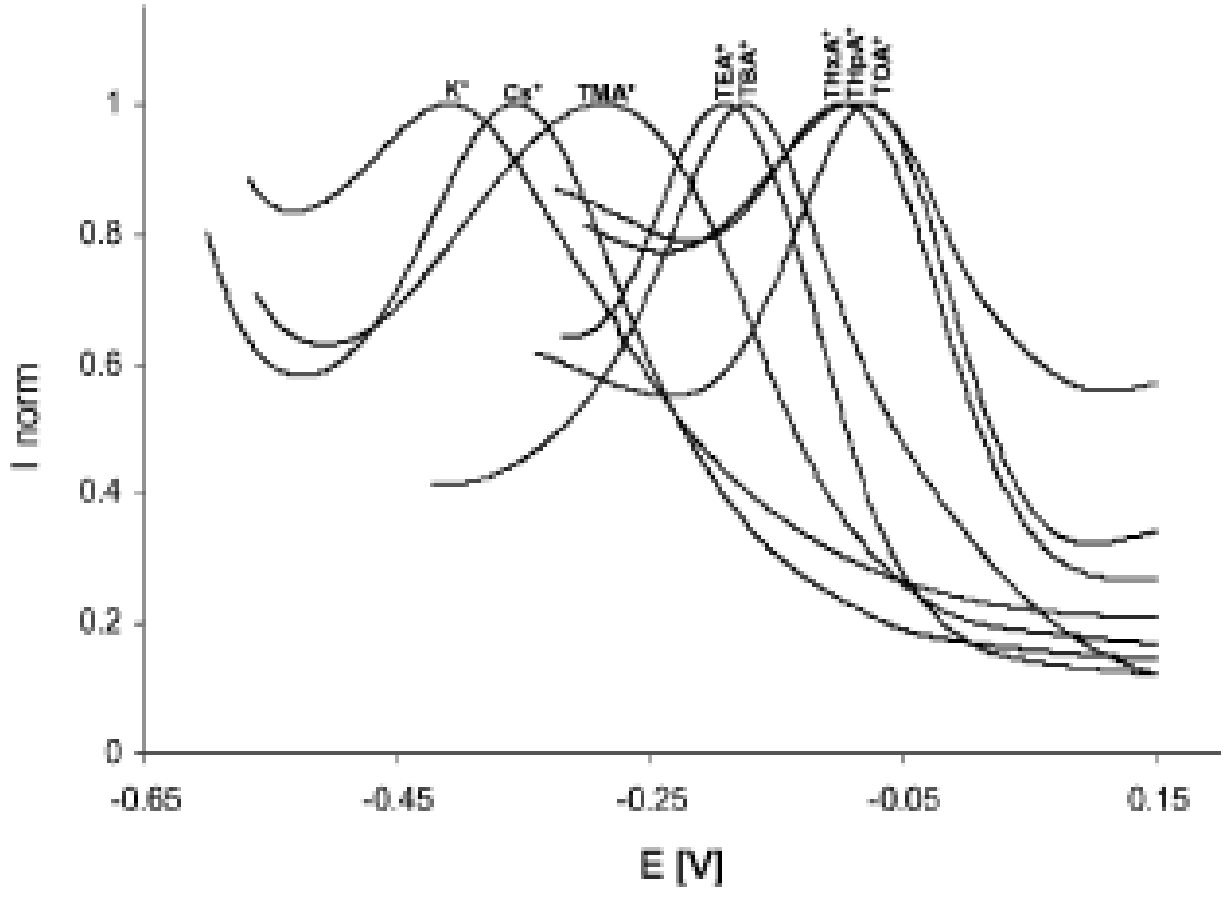
$$\rho = \frac{n^2 F^2 S \sqrt{D} c_{Ox}}{RT} R_\Omega \sqrt{f}$$

Effect of the Uncompensated Resistance in Thin-Film Voltammetry



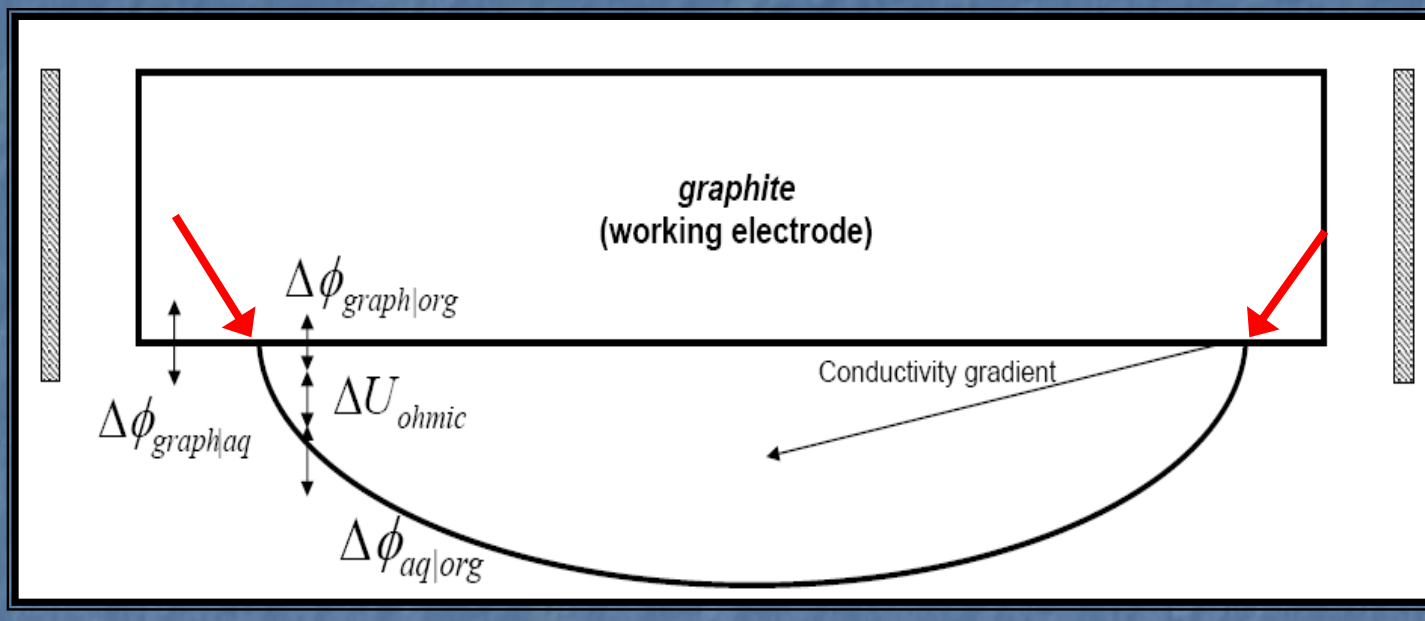
Effect of the SW frequency on the voltammetric response of DMFC





SW voltammograms showing transfer of some monocations across the w|nitrobenzene interface

Mechanistic view of the processes occuring at three-phase electrode



➢INITIALLY-NO ELECTROLYTE IN THE ORGANIC PHASE

➢How (and where) can the reaction in organic phase start?

-The natural partition of the electrolyte from aq. phase enables enough conductivity at the edges of organic phase

$$dmfc(o) + A^-(w) \Leftrightarrow dmfc^+(o) + A^-(o) + 1e^-$$

-Once the reaction in the organic phase starts, then significant ammount of ions is being created in the organic phase

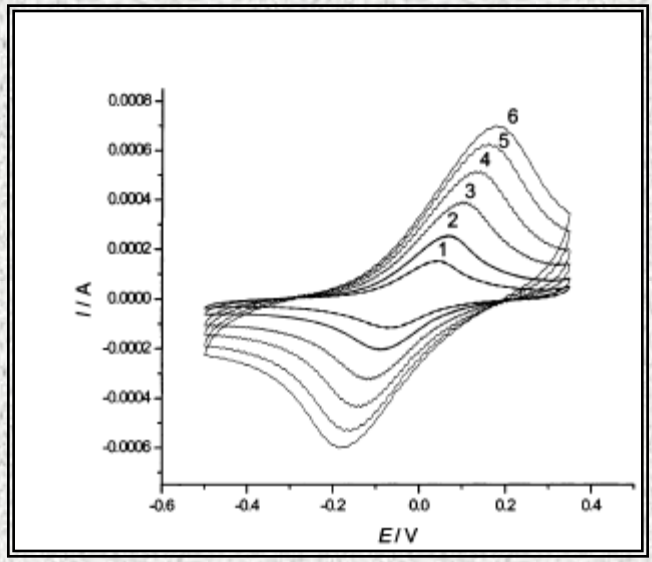
The Ionic content in organic solvent at potential that is 250 mV more negative than the formal potential of the redox system (i.e. at $E(<0) - E^o = -250$ **mV**):

$$c(\text{dmfc+X-})o = c(\text{Salt})w * \varepsilon/2\ [-1+(1+(4 * c(\text{dmfc})o/e * c(\text{salt})w)^{0.5}]$$

$$\varepsilon = \exp(F(E(<0) - E^o)/RT)$$

c(dmfc+X-)org. phase = 5 mM!!!

(for c(dmfc)o = 0.05 M, and c(salt)w = 0.5 M)



➢Expanding of the active organic layer (through diffusion of the ions) :

$$L = k(Dt)^{0.5}$$

I. A-B. Standard Gibbs energies of transfer of some inorganic anions and monoanions of various carboxylic acids

Table 1: Peak potentials E_p, slope of E_p versus concentration of anions in aqueous phase, standard deviation of peak potentials, standard Gibbs energies of ion transfer ΔG^o, and standard deviation of Gibbs energies of all studied anions.

anion	E_p / mV	slope E_p vs. log (c) /mV	$s(E_p)$ / mV	ΔG^o / kJ mol^{-1}	s (ΔG^o) / kJ mol^{-1}
ClO_3^-	2	-55.3	6.43	25.40	0.64
BrO_3^-	60	-58.7	7.17	30.90	0.71
IO_3^-	74	-54.3	8.08	32.40	0.80
IO_4^-	-132	-56.4	2.00	12.50	0.19
OCN^-	45	-50.5	2.45	29.50	0.23
$SeCN^-$	-136	-43.0	5.30	11.80	0.53
CN^-	41	-58.1	4.43	29.60	0.45
N_3^-	14	-52.1	3.44	26.80	0.35
Monofluoro acetate	44	-54.4	5.48	29.90	0.54
Difluoro acetate	34	-48.5	3.90	28.90	0.38
Trifluoro acetate	-2	-60.1	1.79	25.30	0.18
Monochloro acetate	36	-51.5	4.73	29.10	0.48
Dichloro acetate	9	-58.0	1.15	26.40	0.10
Trichloro acetate	-66	-60.1	1.97	18.80	0.20
Monobromo acetate	12	-39.3	3.44	26.70	0.35
Dibromo acetate	-7	-59.0	2.00	24.80	0.20
Tribromo acetate	-94	-59.8	1.03	16.00	0.10
Monoiodo acetate	0	-54.6	1.20	25.10	0.10
$HCOO^-$	58	-56.4	2.40	30.60	0.23
H_3CCOO^-	52	-58.0	1.50	30.10	0.13
$H_3CCH_2COO^-$	29	-54.6	0.80	27.98	0.10
$H_3C(CH_2)_2COO^-$	11	-53.1	2.20	26.25	0.21
$H_3C(CH_2)_3COO^-$	-31	-63.5	2.80	22.30	0.26
$H_3C(CH_2)_4COO^-$	-75	-60.3	1.40	18.10	0.12
$H_3C(CH_2)_5COO^-$	-115	-55.2	1.80	14.20	0.16
$H_3C(CH_2)_6COO^-$	-125	-57.4	4.20	12.64	0.40
$H_3C(CH_2)_7COO^-$	-120	-52.9	3.20	13.40	0.30
$H_3C(CH_2)_8COO^-$	-118	-58.4	2.50	13.60	0.24
Cyclopropane carboxylate	-20	-60.0	1.10	23.25	0.10
Cyclobutane carboxylate	-61	-57.8	1.40	19.30	0.12
Cyclopentane carboxylate	-100	-63.2	1.60	15.54	0.15
Cyclohexane carboxylate	-131	-56.8	2.80	12.54	0.26
Cycloheptane carboxylate	-155	-55.4	2.00	10.22	0.19

- 6 measurements have been performed for one concentration of each anion

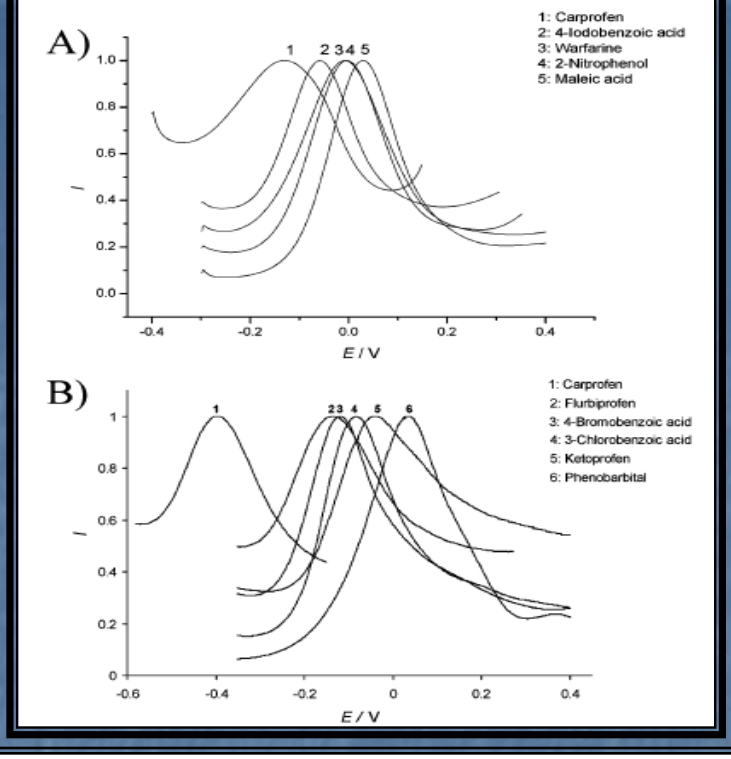
s (E_p) is the standard deviation of SW peak potential

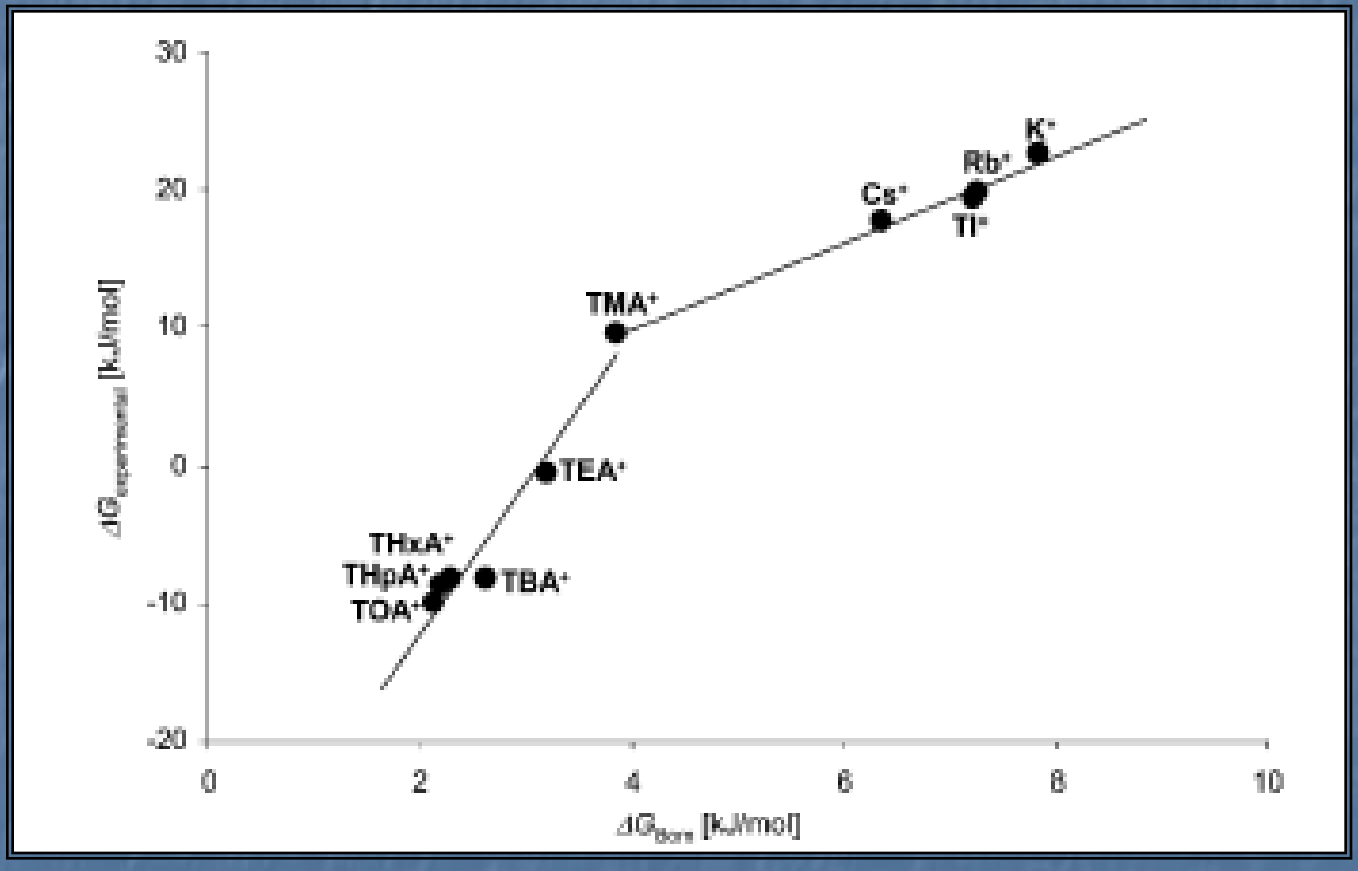
s (ΔG^o) is the standard deviation of Gibbs free energy

TABLE 1: Data of the Lipophilicities of the Investigated Peptides

peptide anions	$\Delta\phi^{\theta}$/V[a]	ΔG^{θ}/kJ mol^{-1}[b]	log P[c]	slope E_p vs log[c]/mV[d]
		(A)		
Trp$^-$[e]	0.115	10.80	−1.90	−64
Trp-Ala$^-$	0.165	15.75	−2.75	−80
Trp-Gly$^-$	0.162	15.60	−2.73	−73
Trp-Val$^-$	0.120	11.60	−2.05	−75
Trp-Leu$^-$	0.100	9.50	−1.66	−73
Trp-Tyr$^-$	0.075	7.40	−1.30	−65
Trp-Phe$^-$	0.055	5.30	−0.93	−77
Trp-Trp$^-$	0.05	4.80	−0.85	−70
Trp-Gly-Gly$^-$	0.165	15.80	−2.75	−75
Trp-Gly-Tyr$^-$	0.155	15.00	−2.65	−74
Trp-Gly-Gly-Tyr$^-$	0.160	15.50	−2.70	−74
		(B)		
Leu-Leu$^-$	0.245	23.70	−4.15	−71
Leu-Leu-Ala$^-$	0.293	28.20	−4.95	−57
Leu-Leu-Gly$^-$	0.290	28.00	−4.91	−80
Leu-Leu-Leu$^-$	0.240	23.20	−4.05	−80
Leu-Leu-Tyr$^-$	0.205	19.70	−3.45	−56
Leu-Leu-Phe$^-$	0.180	17.50	−3.05	−64
Leu-Gly-Phe	0.275	26.50	−4.65	−65
		(C)		
Gly-Phe$^-$	0.260	25.00	−4.40	−59
Gly-Phe-Ala$^-$	0.285	27.50	−4.80	−75
Gly-Phe-Gly$^-$	0.265	25.60	−4.50	−63
Gly-Phe-Tyr$^-$	0.210	20.20	−3.55	−72
Gly-Phe-Phe$^-$	0.208	20.15	−3.53	−70
Phe-Gly-Gly$^-$	0.300	29.00	−5.10	−55
		(D)		
Gly-Gly$^-$[e]	0.280	27.00	−4.75	−49
Gly-Gly-Val$^-$	0.275	26.40	−4.60	−57
Gly-Gly-Leu$^-$	0.280	26.80	−4.70	−56
Gly-Gly-Tyr$^-$	0.300	29.00	−5.10	−57
Gly-Gly-Phe$^-$	0.270	26.00	−4.55	−58
Gly-Gly-Trp$^-$	0.195	19.00	−3.35	−56
Gly-Leu-Gly$^-$	0.280	27.00	−4.75	−49
Gly-Trp-Gly$^-$	0.165	15.80	−2.75	−48
Gly-Tyr-Gly$^-$	0.280	27.10	−4.75	−48
Gly-Leu-Tyr$^-$	0.245	23.40	−4.10	−71
Gly-Leu-Phe$^-$	0.270	26.20	−4.60	−60
Gly-Ala-Phe$^-$	0.285	27.40	−4.80	−70
		(E)		
Tyr-Ala-Gly$^-$	0.260	24.90	−4.40	−48
Tyr-Ala-Gly-Phe-Leu$^-$	0.175	16.60	−2.90	−50
Tyr-Ala-Gly-Leu-Arg$^-$	0.175	17.10	−3.00	−78
Tyr-Ala-Gly-Phe-Met$^-$	0.190	18.40	−3.30	−61
Tyr-Ala-Gly-Met-Phe-Glycinol$^-$	0.260	24.90	−4.40	−48
Tyr-Lys-Thr$^-$	0.255	24.60	−4.30	−59
Lys-Tyr-Thr$^-$	0.310	30.00	−5.25	−58
		(F) Amino Acid Anions[e]		
Gly$^-$	0.275	26.60	−4.65	−54
Ala$^-$	0.285	27.50	−4.80	−58
Val$^-$	0.278	26.80	−4.70	−52
Leu$^-$	0.245	23.90	−4.20	−66
Phe$^-$	0.215	21.00	−3.70	−60
Tyr$^-$	0.220	21.20	−3.72	−64
Met$^-$	0.255	24.50	−4.30	−56
Trp$^-$	0.115	10.80	−1.90	−64
Lys$^-$	0.283	27.30	−4.78	−48
Pro$^-$	0.305	29.50	−5.20	−59
His$^-$	0.29	27.70	−4.85	−63

[a] Standard potential differences at the W|NB interface ($\Delta\phi^{\theta}$). [b] Standard Gibbs energies of ion transfer (ΔG^{θ}). [c] Logarithm of the ion partition coefficients (log P). [d] Slopes of the dependencies of the peak potentials vs logarithm of the concentration of peptide anions in the water phase (E_p vs log[c]) evaluated from the square-wave voltammetric responses of dmfc at the three-phase electrode. [e] Data taken from ref 16.





Comparison between experimentally determined and the estimated values by using the electrostatic Born theory

$\Delta G^{NB^{\circ}}_{W\,Cat^{+}}$

The Ionic content in organic solvent at potential that is 250 mV more negative than the Standard redox potential (i.e. at $E(<0) - E^{o} = -250$ mV):

$$c(\mathrm{dmfc^{+}X^{-}})_{o} = c(\mathrm{Salt})_{w} * \varepsilon/2\ [-1+(1+(4*c(\mathrm{dmfc})o/\varepsilon * c(\mathrm{salt})_{w})^{0.5}]$$

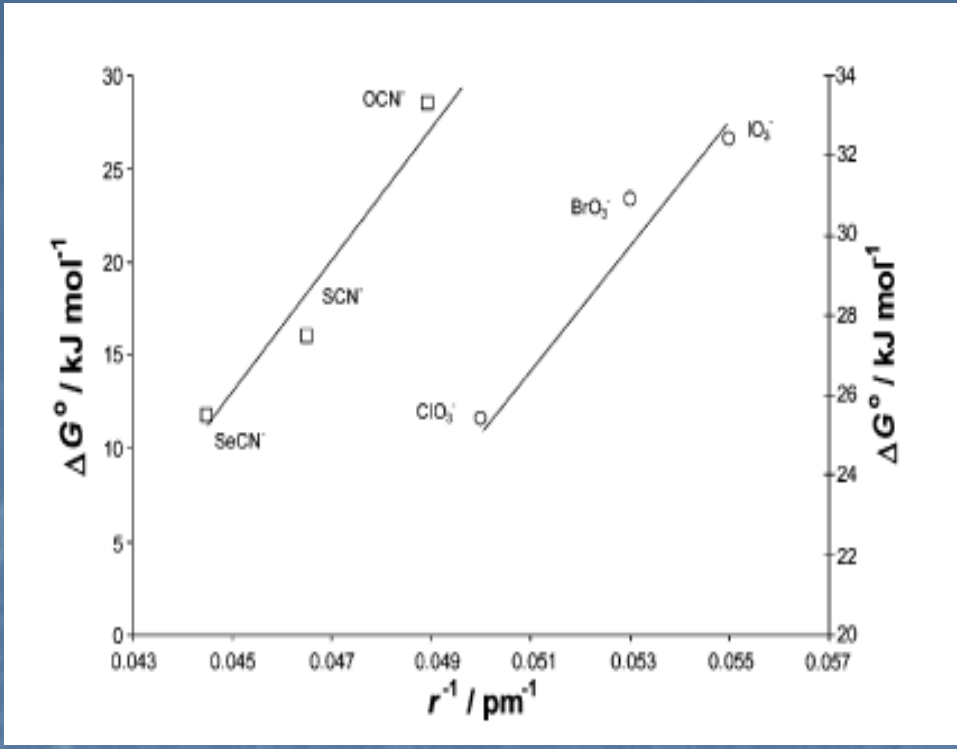
$$\varepsilon = \exp(F(E(<0) - E^{o})/RT)$$

$c(\mathrm{dmfc^{+}X^{-}})_{\text{org. phase}} = 5$ mM!!!

(for $c(\mathrm{dmfc})_{o} = 0.05$ M, and $c(\mathrm{salt})_{w} = 0.5$ M)

Distance that can be reached by diffusion:

$$L = (Dt)^{0.5}$$


ΔG° / kJ mol-1
ΔG° / kJ mol-1
r-1 / pm-1
OCN-
SCN-
SeCN-
ClO3-
BrO3-
IO3-
30
25
20
15
10
5
0
34
32
30
28
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24
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20
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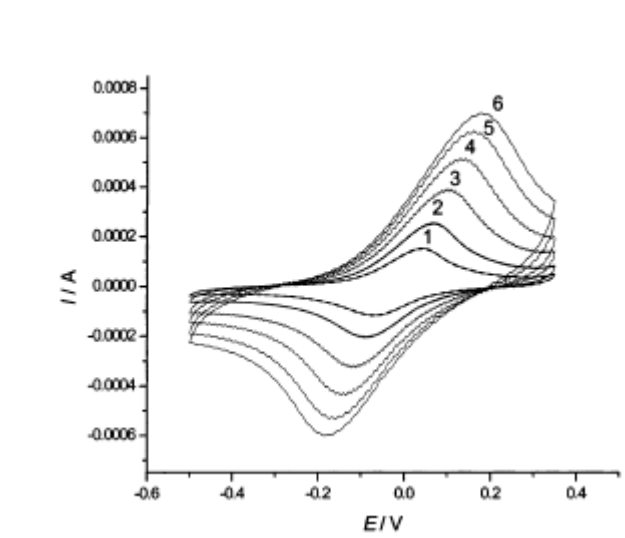
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E / V
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0.0006
0.0004
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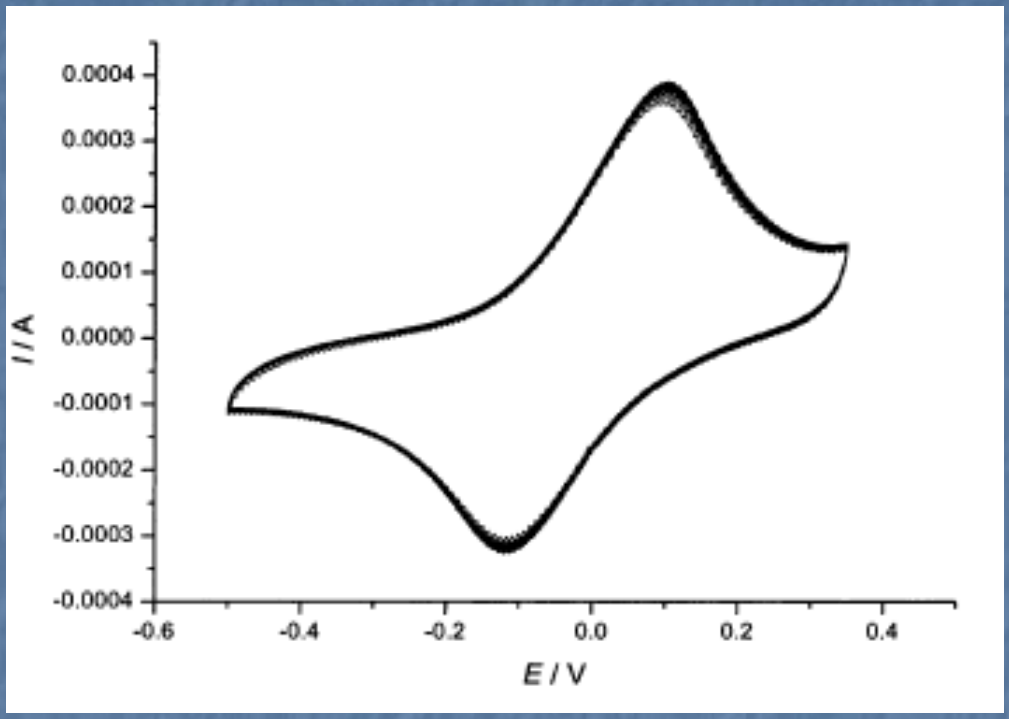
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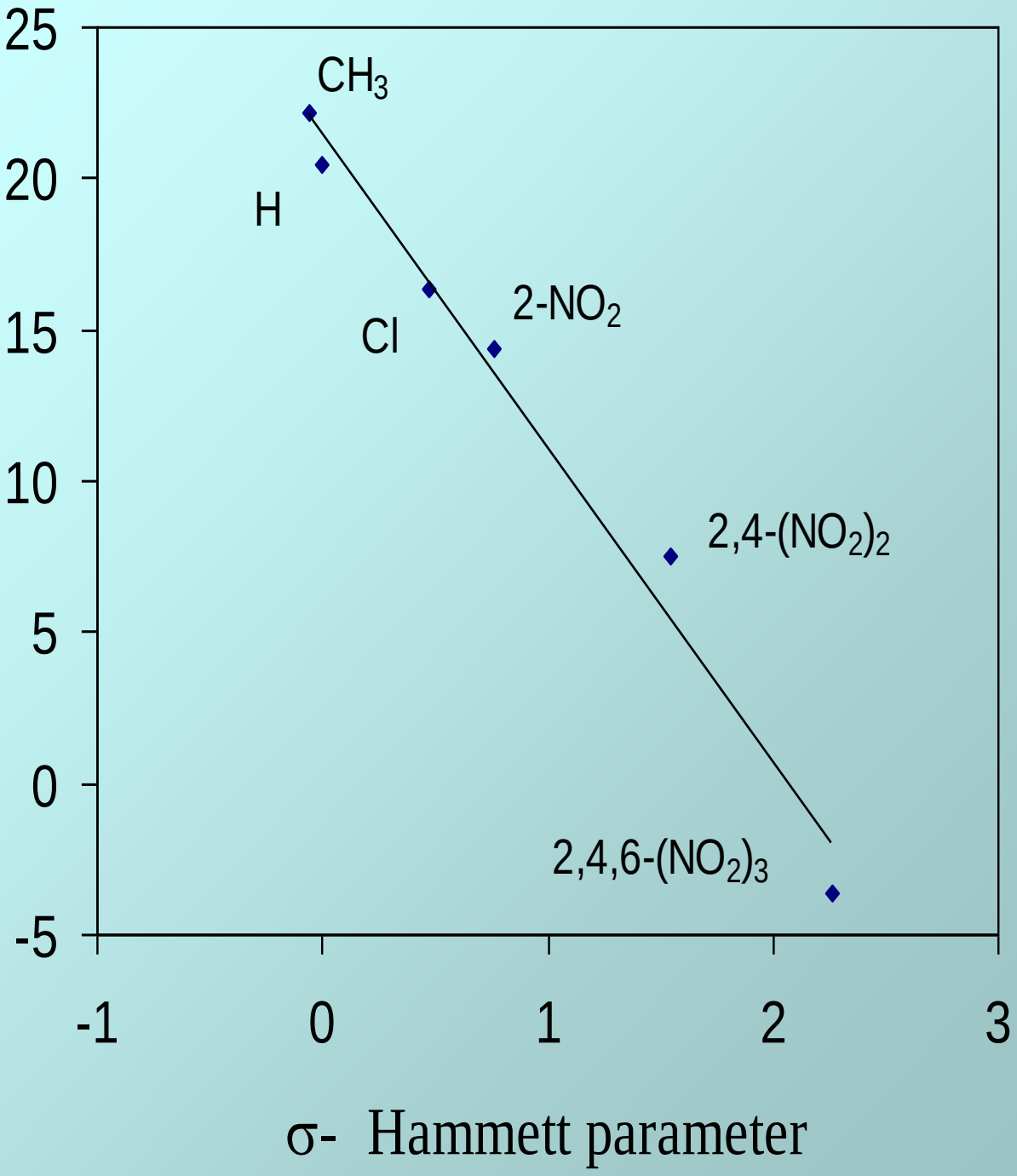
-0.2
0.0
0.2
0.4
E / V


25
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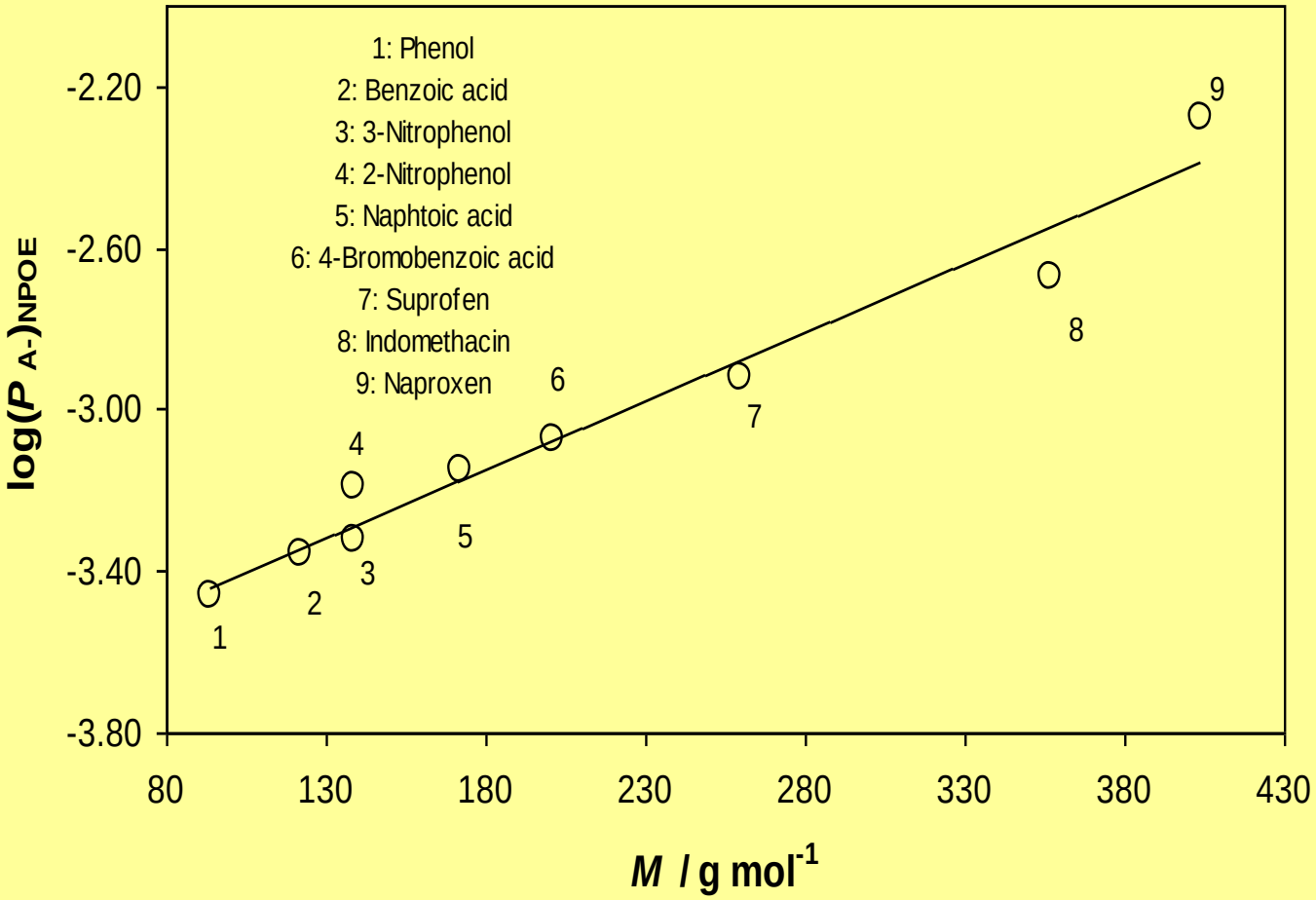
15
10
5
0
-5
-1
0
1
2
3
CH3
H
Cl
2-NO2
2,4-(NO2)2
2,4,6-(NO2)3
σ- Hammett parameter


1: Phenol
2: Benzoic acid
3: 3-Nitrophenol
4: 2-Nitrophenol
5: Naphtoic acid
6: 4-Bromobenzoic acid
7: Suprofen
8: Indomethacin
9: Naproxen
-2.20
-2.60
-3.00
-3.40
-3.80
80
130
180
230
280
330
380
430
log(P A-)NPOE
M / g mol-1